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NITRATE REMOVAL FROM DRINKING WATER IN GLENDALE, ARIZONA

by

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Cooperative Agreement No. CR-807939

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16. ABSTRACT

A 15-month pilot-scale study of nitrate removal from drinking water by ion exchange (IX), reverse osmosis (RO), and electrodialysis (ED) was carried out in Glendale, Arizona, where the raw water contained 18 to 25 mg/L NO_3-N. The experiments were carried out using the University of Houston/U.S. EPA Mobile Drinking Water Treatment Research Facility.

All three processes could readily reduce the nitrate level far below the maximum contaminant level of 10 mg/L NO_3-N. For the desalting processes, the polyamide RO membrane performed better than cellulose triacetate on the basis of nitrate rejection--94% compared with 76%, respectively. However, ED performed better than either RO membrane by producing 96% nitrate rejection at 76% recovery. Various flow rates, commercial resins, and sulfate concentrations were tried during the IX exhaustion tests. Of these, only the sulfate concentration was important: As it increased the time to nitrate breakthrough was sharply reduced.

Regeneration of the nitrate-laden resin was studied extensively using complete regeneration, partial regeneration, and regenerant reuse. For complete regeneration, the more dilute the regenerant, the more efficient it was. Partial regeneration, consumed 37% less NaCl than the most efficient complete regeneration. Regenerant reuse and counterflow regeneration were not effective.

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxic Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direst the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

Nitrate contamination above the allowable level specified in the Safe Drinking Water Act is being found in an ever increasing number of the nation's groundwaters primarily as a result of man's necessary activities including fertilization and wastewater treatment. This report describes nitrate-removal studies done in a typical field location with a mobile pilot plant. The results of this research on ion exchange, reverse osmosis and electrodialysis will be helpful in solving some of the many nitrate contamination problems in the United States, particularly in small communities.

Francis T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

A 15-month pilot-scale study of ion exchange (IX), reverse osmosis (RO), and electrodialysis (ED) for nitrate removal from well water was carried out in Glendale, Arizona, where 10 of 31 wells had been shut down because of excess nitrates. The raw water contained 18 to 25 mg/L NO_3-N, 43 mg/L sulfate, and it had a TDS of 530 mg/L.

All three processes (IX, RO, and ED) could readily reduce nitrates to below the MCL. Rough cost estimates, however, indicated that the desalting processes would be much more expensive than chloride ion exchange. The relative capital plus operating cost estimates for a 1.0 mgd (3,800-m^3/day) plant producing a 7.0-mg/L nitrate-N product water are $1.00/1000 gal (3.8 m^3) for RO, $0.85/1000 gal for ED, and $0.30/1000 gal for ion exchange. Although ion exchange is by far the lowest cost process, it produces a high chloride product water with about 500 mg/L TDS, whereas the blended ED and RO product waters would contain only about 180 mg/L TDS. Also, the disposal of the ion exchange wastewater (NaCl + $NaNO_3$ brine) is potentially a much larger problem than the disposal of RO or EDR brine. The polyamide RO membrane performed better than cellulose triacetate on the basis of nitrate rejection (94% compared with 76%), but ED, which produced 96% rejection at 76% recovery, performed better than either membrane. The results of this study indicate that, overall, ED is slightly superior to RO when estimated costs, nitrate rejection, and degree of pretreatment are taken into consideration. Wastewater disposal costs are not included in the estimates.

Because of its simplicity and low cost, ion exchange with strong base resins in the chloride form was studied in detail. Various resins, flow rates, and sulfate concentrations were tried during the column exhaustion tests. Of these variables, only sulfate concentration was important in the ranges studied. As it increased, the nitrate removal capacity, bed volumes (BV) to nitrate breakthrough, was sharply reduced; and the nitrate elution peak sharply increased. With the standard, strong-base anion resins tested, nitrate always broke through before sulfate, which caused nitrate to peak. Note, however, that resins now being developed by other investigators using triethyl, tripropyl, and tributyl quaternary amine functionality will cause sulfate to break through first and presumably eliminate this nitrate peaking problem.

Regeneration of the nitrate-laden resin was studied extensively using the complete and partial regeneration techniques with various NaCl concentrations. The reuse of spent regenerant was attempted, as was counterflow (upflow) regeneration. These measures were ineffective but worthy of further study. For complete regeneration (i.e., the removal of

>95% of the adsorbed nitrate), the more dilute the regenerant, the more efficient it was. For example, 0.25 N NaCl required 3.0 equivalents of Cl/equivalent of resin, whereas 1.0 N NaCl required 180% of this value. Partial regeneration (i.e., the removal of about 60% of the adsorbed nitrate followed by complete mixing of the bed and high-nitrate leakage exhaustion) was considerably more efficient than complete regeneration. For the production of 1.0 mgd (3,800 m^3/day) of 7.0 mg/L nitrate-N product water, partial regeneration consumes 890 lb/day (404 kg/day) less salt and produces a more concentrated wastewater with much less volume.

During the course of this study, it was discovered that a measurable pH change resulting from carbonate elution accompanies and therefore signals nitrate breakthrough from completely regenerated beds. This phenomenon needs further study as a function of (1) the nitrate/sulfate selectivity of the resin, (2) the bicarbonate and sulfate concentration of the water, and (3) the partially regenerated condition of the bed.

The recommended method of treatment for 1.0 mgd (3800 m^3/day) of the Glendale water is chloride ion exchange followed by partial regeneration. This presumes that disposal can be arranged for 11,000 gal/day (42 m^3/day) of spent regenerant containing 30,000 mg/L TDS and 5200 mg/L nitrate-N.

This report is submitted in partial fulfillment of grant number CR-807939-02 under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period from March 1981 to December 1983, and work was completed as of April 1985.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

Alk	-- Carbonate Alkalinity
alpha S/N	-- sulfate/nitrate separation factor
alpha N/Cl	-- nitrate/chloride separation factor
ASB-1	-- designation for type -1 resin from Sybron/Ionac
ASB-2	-- designation for type-2 resin from Sybron/Ionac
BV(N)	-- bed volumes to nitrate breakthrough
Cap	-- resin exchange capacity
Dowex-11	-- designation for type-1 resin from Dow Chemical
EBCT	-- empty bed contact time, min.
ED	-- electrodialysis
EDR	-- electrodialysis with current reversal
eq., equiv.	-- equivalent
Gel	-- Gel-type porosity of resin
HCHO	-- formaldehyde
Iso	-- isoporous (more porous than gel)
IX	-- ion exchange
MCL	-- maximum contaminant level
MR	-- macroporous
NO_3-N	-- nitrate concentration measured as nitrogen
Quat	-- quaternary amine

ABBREVIATIONS

R -- complete regeneration

RP -- partial regeneration

RPU -- upflow partial regeneration

RS -- regeneration with spent regenerant containing nitrate and sulfate

R2 -- polishing regeneration following a spent regeneration

SBA -- strong base anion

SDI -- silt density index

SHMP -- sodium hexa meta phosphate

STY-DVB -- styrene divinylbenzene copolymer

TDS -- total dissolved solids

TH -- total hardness

TSS -- total suspended solids

type I -- resin with $N(CH_3)_3$ functionality

type II -- resin with $N(CH_3)_2$ $(C_2H_4\ OH)$ functionality

SYMBOLS

C_F, C_0 -- concentration of species in feed

C_p -- concentration of species in product

pKa -- negative logarithm of protolysis constant

x_i -- equivalent fraction of ion i in liquid phase

y_i -- equivalent fraction of ion i in solid phase

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SECTION 1

INTRODUCTION

MOBILE DRINKING WATER RESEARCH FACILITY

The EPA's National Interim Primary Drinking Water Regulations (1976) established maximum contaminant levels (MCL's) for potentially hazardous inorganic ions in drinking water. Several thousand public ground water supplies in small communities throughout the United States contain one or more of these contaminants (fluoride, nitrate, arsenic, selenium, radium, barium, or chromium) in excess of the MCL.

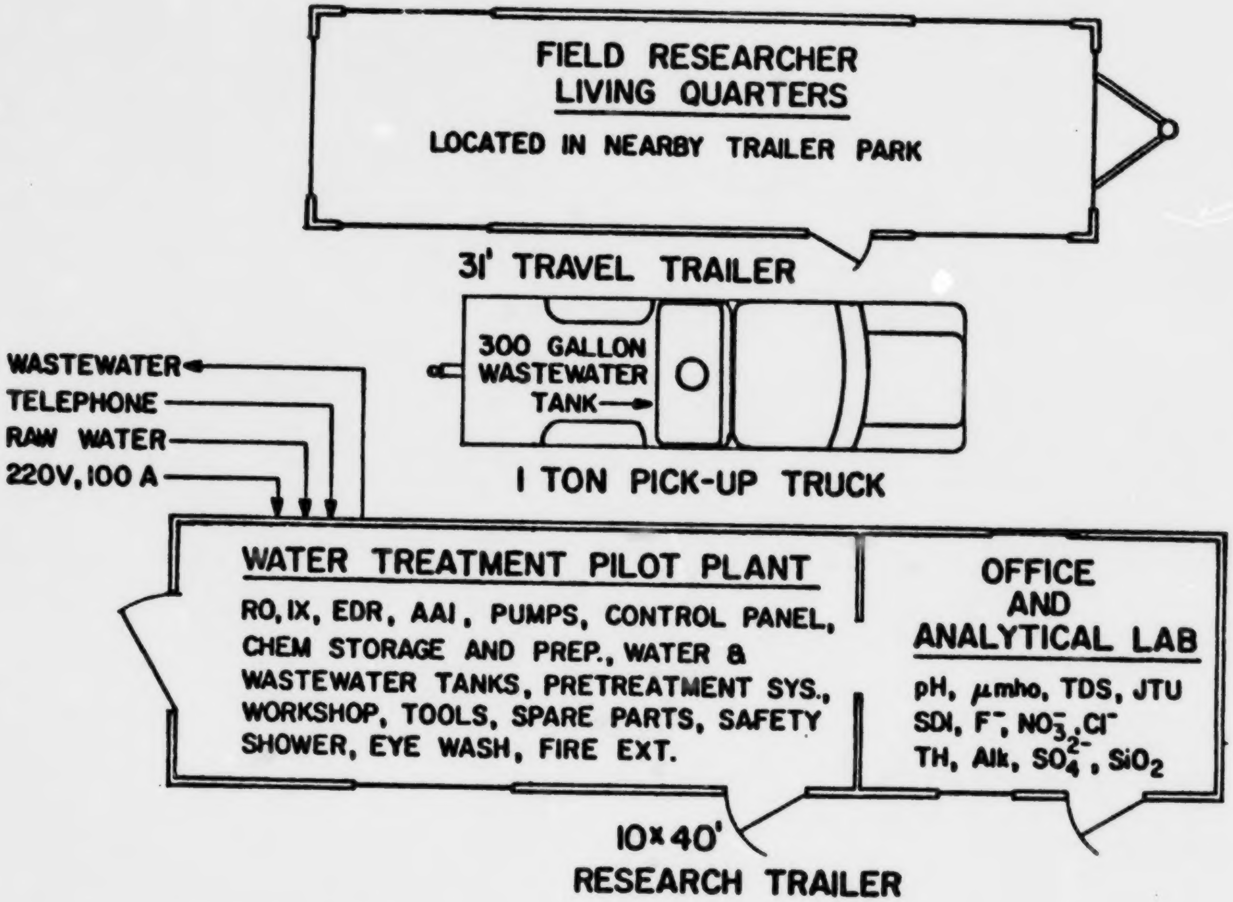
With EPA funding, researchers at the University of Houston have undertaken a long-term project to evaluate single-contaminant removal and desalting processes for the purification of contaminated water supplies. A mobile drinking water treatment research facility, outfitted with pilot plant and laboratory equipment for alumina adsorption, ion exchange, reverse osmosis, and electrodialysis, was designed and built at the University of Houston in 1978-80 (see Figures 1-3). This facility is described in detail in an earlier report by Clifford and Bilimoria [1]. The facility is being used in a series of on-site studies at contaminated wells in small communities.

The first location (April 1980 to March 1981) of the facility was Taylor, Texas, (population 13,000), where fluoride removal from a 3.0-ppm F^-, 1100 mg/L TDS groundwater was studied using activated alumina, electrodialysis, and reverse osmosis. A separate report "Fluoride Removal from Drinking Water in Taylor, Texas" has been prepared [2].

In March 1981, the mobile research facility was moved to Glendale, Arizona (population 90,000), a suburb of Phoenix where 10 of their 32 wells had been shut down because of nitrate levels exceeding the 10-mg/L MCL. EDR, RO, and IX were studied for removal of nitrate from a 19-mg/L NO_3-N, 500-mg/l TDS well water. The Glendale work is the subject of this report.

THE NITRATE PROBLEM

Nitrate nitrogen (NO_3-N) at concentrations above the 10-mg/L MCL is found in ground water supplies in rural, suburban, and even some urban areas throughout the United States. Nitrate contamination of drinking water presents a health hazard because nitrate can be reduced to toxic nitrite ion in the gastrointestinal tract of humans and other mammals.


FIELD RESEARCHER
LIVING QUARTERS
LOCATED IN NEARBY TRAILER PARK
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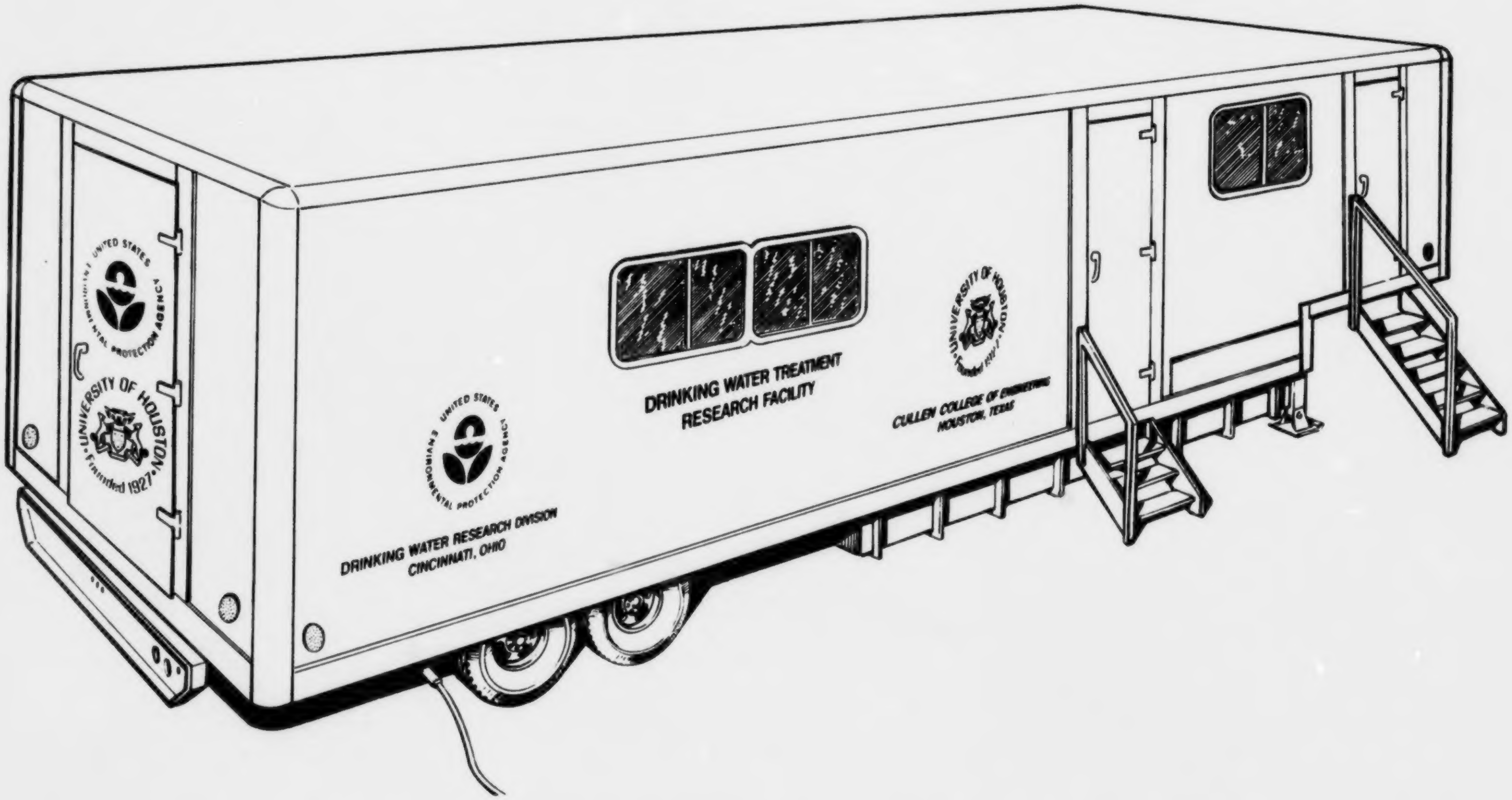
WASTEWATER
TANK
1 TON PICK-UP TRUCK
WASTEWATER
TELEPHONE
RAW WATER
220V, 100 A
WATER TREATMENT PILOT PLANT
RO, IX, EDR, AAI, PUMPS, CONTROL PANEL, CHEM STORAGE AND PREP., WATER & WASTEWATER TANKS, PRETREATMENT SYS., WORKSHOP, TOOLS, SPARE PARTS, SAFETY SHOWER, EYE WASH, FIRE EXT.
OFFICE
AND
ANALYTICAL LAB
pH, µmho, TDS, JTU
SDI, F^-, NO_3^-, Cl^-
TH, Alk, SO_4^{2-}, SiO_2
10×40'
RESEARCH TRAILER

Figure 1. Mobile research concept including transportable pilot plant/ laboratory, travel trailer, and pickup truck.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DRINKING WATER RESEARCH DIVISION
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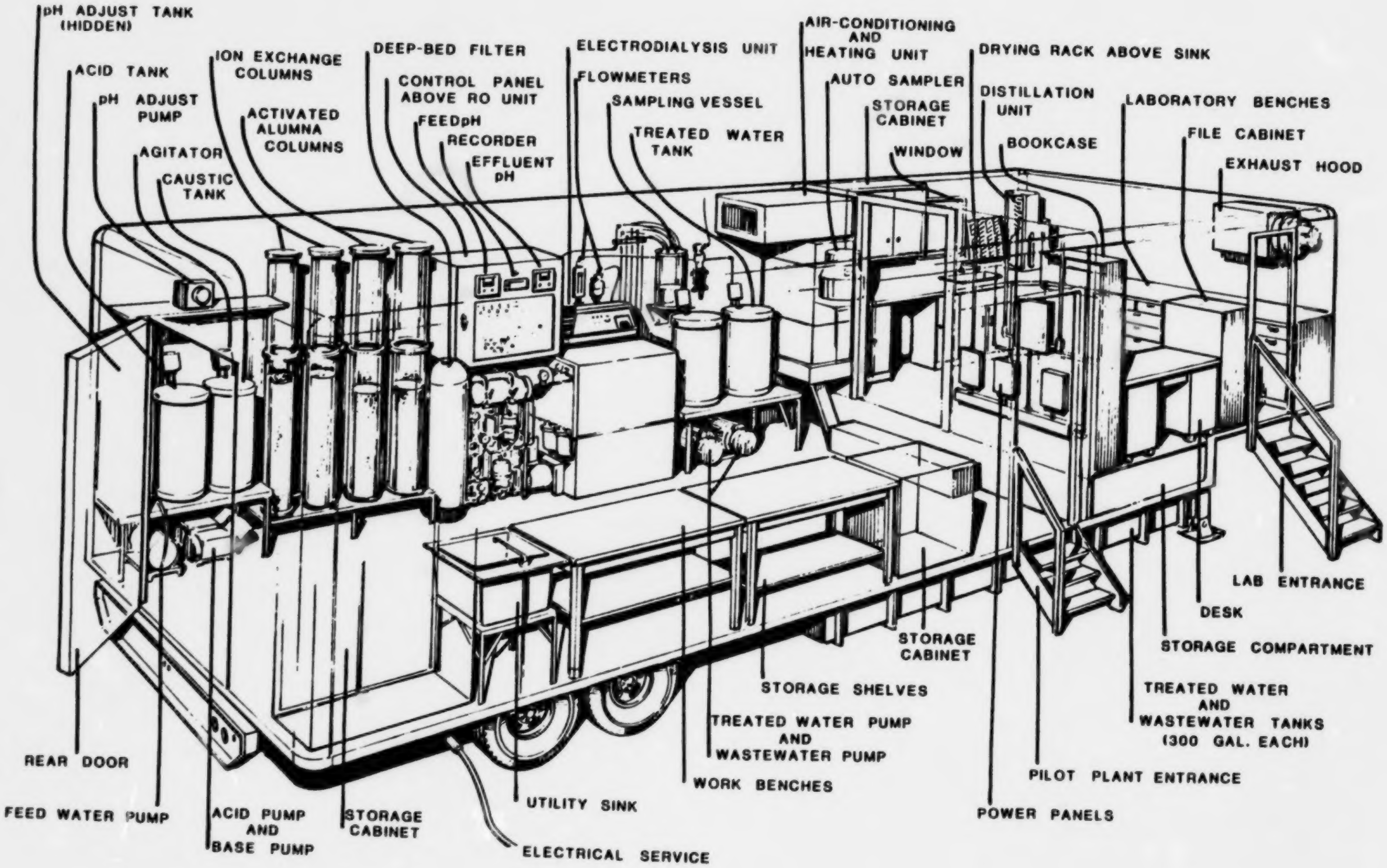
DRINKING WATER TREATMENT
RESEARCH FACILITY
CULLEN COLLEGE OF ENGINEERING
HOUSTON, TEXAS

Figure 2. Exterior perspective drawing of mobile research facility located in Glendale, Arizona for this study of nitrate removal from well water.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pH ADJUST PUMP
AGITATOR
CAUSTIC TANK
ION EXCHANGE COLUMNS
ACTIVATED ALUMNA COLUMNS
DEEP-BED FILTER
CONTROL PANEL ABOVE RO UNIT
FEEDpH
RECORDER
EFFLUENT pH
ELECTRODIALYSIS UNIT
FLOWMETERS
SAMPLING VESSEL
TREATED WATER TANK
AIR-CONDITIONING AND HEATING UNIT
AUTO SAMPLER
STORAGE CABINET
WINDOW
DRYING RACK ABOVE SINK
DISTILLATION UNIT
BOOKCASE
LABORATORY BENCHES
FILE CABINET
EXHAUST HOOD
LAB ENTRANCE
DESK
STORAGE COMPARTMENT
TREATED WATER AND WASTEWATER TANKS (300 GAL. EACH)
PILOT PLANT ENTRANCE
POWER PANELS
STORAGE CABINET
STORAGE SHELVES
TREATED WATER PUMP AND WASTEWATER PUMP
WORK BENCHES
UTILITY SINK
ELECTRICAL SERVICE
STORAGE CABINET
ACID PUMP AND BASE PUMP
FEED WATER PUMP
REAR DOOR

Figure 3. Interior layout of the UH/EPA Drinking Water Treatment Research Facility showing both the pilot plant and laboratory equipment.

Nitrite causes methemoglobinemia, a sometimes fatal disease to which infants and cattle are particularly susceptible. Sources of groundwater nitrate include unused fertilizer, nitrifed sewage, precipitation, dustfall, biological fixation, and geologic deposits. Precipitation and dustfall represent diffuse sources that return nitrogen in ammonia and nitrate form to the land surface. Increases in nitrogen levels from these sources are influenced by man's activity. The combustion of fossil fuels and the volatilization of ammonia during fertilization can substantially increase nitrogen concentrations in both rainfall and dustfall. Nitrate-contaminated groundwater may be found in areas where microbial denitrification is insufficient to remove the nitrates applied to the surface.

RESEARCH OBJECTIVES

The specific objectives of the Glendale, Arizona, work were:

1. To compare, on the basis of technical feasibility and process economics, reverse osmosis, electrodialysis, and strong-base, chloride-form anion exchange for the removal of groundwater nitrate from Glendale's Well No. 1 (18-23 mg NO_3-N/L).

2. For ion exchange,

   a. To evaluate the effects of resin type, sulfate concentration, and flow rate on the exhaustion process.

   b. To evaluate the effects of NaCl concentration, regeneration level, flow direction, and spent regenerant reuse on the regeneration process.

   c. To optimize the design of a single-bed, chloride-ion-exchange process using complete regeneration.

   d. To optimize the design of a single-bed, chloride-ion-exchange process using partial regeneration.

PREVIOUS WORK ON NITRATE REMOVAL

Clifford and Weber [3] studied sulfate/nitrate, chloride/nitrate and bicarbonate/nitrate selectivity of 32 commercially available anion resins--13 weak-base and 19 strong-base. They correlated selectivity to the following resin properties: polymer matrix, functionality, porosity, capacity, pKa, and type. The selectivity sequence was found to be sulfate > nitrate > chloride > bicarbonate. Although all the resins showed a sulfate preference at 0.005 N, the sulfate/nitrate separation factors, alpha S/N, varied widely. The most important factor influencing alpha S/N was shown to be polymer matrix. If the electrostatically active N atoms are in the continuous polymer structure, as they are for all but the polystyrene resins where the active N is pendant on the polymer structure, the resin is highly sulfate selective. This strong preference for the divalent anion was attributed to the guaranteed proximity of N atoms in the polymer matrix. Sulfate selectivity is reduced for the polystyrene-divinylbenzene resins because the pendant functional groups are less likely to be close enough together to satisfy divalent counterions.

In multicomponent column studies, Clifford and Weber showed that alpha N/Cl was most important in determing nitrate removal efficiency and that alpha S/N was nearly irrelevant. In fact, higher alphaS/N gave slightly increased nitrate removal efficiency. These results were found to be in accord with predictions made from Multicomponent Chromatography Theory [4] and have been explained by Clifford in recent publications [5,6]. Since sulfate is always preferred, it is adsorbed first, forming a sulfate-rich zone at the inlet end of the bed. Further down the column, since the feed solution has been depleted of sulfate, the chloride and nitrate ions compete for IX sites in a second zone. Therefore, it is the nitrate/chloride selectivity that governs the fraction of nitrate on the column at breakthrough since that nitrate is contained almost exclusively in the second zone. Note that sulfate is not always the most preferred of the common ions. When ionic strength is high (e.g., 0.02 M), nitrate may be preferred to sulfate, as was found by Guter [7] and as expected from theory (see Helfferich [8] electroselectivity reversal, p. 156).

Clifford [3] classified anion resins as acceptable or unacceptable for removal of nitrate from water containing sulfate, chloride, and bicarbonate. The list is as follows:

ACCEPTABLE

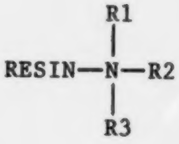
STY-DVB, polyamine, gel resins
STY-DVB, tertiary amine, MR resins
STY-DVB, quaternary (I & II) amines, gel, MR and iso
Acrylic-amine, polyamine, MR resins
Phenol-HCHO, polyamine, MR resins

UNACCEPTABLE (due to low alpha N/Cl)

Epoxy-amine, polyamine, gel resins
Acrylic amine, tertiary amine, gel resins
Aliphatic amine, polyamine gel resins (excessive organic bleed)

Guter [7] has studied removal of nitrate from a contaminated well in McFarland, California. The water there has about the same nitrate concentration but seven times greater sulfate concentration than Glendale water. Guter's studies included reverse osmosis, ion exchange, and a combination of reverse osmosis followed by ion exchange. The RO system operation was plagued by electrical and mechanical failures, making it undesirable for well-site nitrate removal in a small community with few or no maintenance personnel. A particularly serious problem was the deterioration of the RO seals as a result of the repeated on-off cycling of the unit due to water demand. Cost of the RO process was estimated to be excessively high, about \$0.99/1000 gallons of product water.

Guter also investigated the chemistry of sulfate/nitrate selectivity. Using experimental resins made by Diamond Shamrock, selective resins could be synthesized by increasing the size of the R groups about the quaternary ammonium nitrogen in the structure:



$$\begin{array}{ccc} & R1 & \\ & | & \\ \text{RESIN}— & N & —\text{R2} \\ & | & \\ & R3 & \end{array}$$

This was true only for non-polar R groups. His results are completely in accord with those of Clifford and Weber [3] who showed that nitrate selectivity is highest in hydrophobic (non-polar) resins and resins with low sulfate selectivity due to relatively large N separation distance. Despite the focus of Guter's research on new nitrate selective resins, he used a commercially available strong-base ion-exchange resin, Duolite A-101D, for most of the pilot plant studies. This resin has a STY-DVB polymer matrix and a quaternary, type I functionality, i.e. "acceptable" for nitrate removal by the Clifford-Weber criteria. The nitrate selective resins have not been abandoned, however, and future pilot studies with them are planned. Of special interest are the triethyl and tripropyl functionality resins which have nearly the same capacity as the type I trimethyl resins but which prefer nitrate over sulfate.

Of particular interest in Guter's pilot plant work is his study of partial regeneration which was also suggested by Gauntlett [9]. In the typical IX process, exhaustion of a resin bed is followed by regeneration with brine until the entire bed is restored to the chloride form. This process is subject to diminishing returns, with much more regenerant solution required per equivalent of IX sites converted toward the completion of regeneration than at the beginning. Guter showed that it is possible to achieve the desired nitrate removal with a process involving only partial regeneration of the resin. The process is economically attractive because it substantially reduces the NaCl requirement and the amount of waste brine produced. The disadvantage (or advantage, depending on one's point of view) of partial regeneration is the 6-14 ppm NO_3-N leakage which results from the nitrate left on the resin.

At least two previous studies of nitrate removal by reverse osmosis have been reported. Fox [10] studied the performance of two types of RO membranes--DuPont Permasep hollow fiber aramid membrane and the Osmonic Sepralator spiral wound cellulose acetate membrane--for removal of As, Se, F, NO_3-N, Cd, Pb, and Cr from spiked well water. Nitrate rejection was 80--90% (independent of pH) for the aramid membrane, 51--95% (pH dependent) for the cellulose acetate membrane. Product water recovery was 40--50% for the aramid and only 3 to 8% for the cellulose acetate. Both operated at about 200 psi. Fox demonstrated that both systems could reduce the NO_3-N concentration of a 25 mg/L feed to below the 10 mg/L MCL.

Huxstep [11] compared the performance of spiral wound cellulose acetate membranes for F, As, and NO_3-N removal at high (400 psi) and low (200 psi) pressure. The high pressure system rejected 75--80% of feed water nitrate, while the low pressure system rejected only 6--25%. Each operated with 75% product water recovery. The high pressure system could achieve the MCL for a 46 mg/L NO_3-N feed, but the low pressure system could only effectively treat a 14 mg/L NO_3-N feed.

It is interesting to note that both Fox and Huxstep reported biodegradation or fouling of the cellulose acetate membranes during the nitrate removal studies. Since nitrate supports bacterial growth, it is important to protect cellulose acetate membranes by continuous chlorine disinfection or periodic disinfection with formaldehyde or some other biocide. Aramid (polyamide) membranes are not susceptible to bacterial attack. On the other hand, they are readily attacked by chlorine which must be removed from the feedwater.

SECTION 2

CONCLUSIONS

A 15-month pilot-scale study of ion exchange (IX), reverse osmosis (RO), and electrodialysis (ED) for nitrate removal from well water was carried out in Glendale, Arizona, where 10 of 31 wells had been shut down because of excess nitrates. The raw water contained 18 to 25 mg/L NO_3-N, 43 mg/L sulfate, and it had a TDS of 530 mg/L.

All three processes (IX, RO, and ED) could readily reduce nitrates to far below the MCL of 10 mg/L of nitrate nitrogen. Rough cost estimates, however, indicated that the desalting processes would be much more expensive than chloride ion exchange. The relative capital plus operating cost estimates for a 1.0 mgd (3,800-m^3/day) plant producing a 7.0-mg/L nitrate-N product water are $1.00/1000 gal (3.8 m^3) for RO, $0.85/1000 gal for ED, and $0.30/1000 gal for ion exchange. Wastewater disposal costs are not included in the estimates.

Although ion exchange is by far the lowest cost process, it produces a high chloride product water with about 500 mg/L TDS, whereas the blended ED and RO product waters would contain only about 180 mg/L TDS. Also, the disposal of the ion exchange wastewater ($NaCl + NaNO_3$ brine) is potentially a much larger problem than the disposal of RO or EDR brine.

The polyamide RO membrane performed better than cellulose triacetate on the basis of nitrate rejection (94% compared with 76%), but ED, which produced 96% rejection at 76% recovery, performed better than either membrane. The results of this study indicate that overall, ED is slightly superior to RO when estimated costs, nitrate rejection, and degree of pretreatment are taken into consideration.

Because of its simplicity and low cost, ion exchange with strong base resins in the chloride form was the process studied in the greatest detail. Three different resins (type 1 gel, type 2 gel and type 1 isoporous), two flow rates, and three sulfate concentrations (43, 140, and 310 mg/L) were tried during the column exhaustion tests. Of these variables, only sulfate concentration was important in the ranges studied. As it increased, the nitrate removal capacity, bed volumes (BV) to nitrate breakthrough, was sharply reduced; and the nitrate elution peak sharply increased.

With the standard, strong-base anion resins tested, nitrate always broke through before sulfate, which caused nitrate to peak. Note, however, that resins now being developed by other investigators using triethyl, tripropyl, and tributyl quaternary amine functionality will cause sulfate to break through first and presumably eliminate this nitrate peaking problem.

Regeneration of the nitrate-laden resin was studied extensively using the complete and partial regeneration techniques with NaCl concentrations in the range of 0.25-3.0 N. For complete regeneration (i.e., the removal of >95% of the adsorbed nitrate), the more dilute the regenerant, the more efficient it was. For example, 0.25 N NaCl required 3.0 equivalents of Cl/equivalent of resin, whereas 1.0 N NaCl required 180% of this value.

The fact that dilute salt is more effective than concentrated salt is attributed to two factors: (1) the reversal of divalent ion (sulfate) selectivity at increasing ionic strength, and (2) inefficient utilization of NaCl due to mass transfer limitations at high concentration. The selectivity reversal results in sulfate becoming less and less preferred, and therefore ineffective in driving off nitrate, as the NaCl concentration increases.

Partial regeneration (i.e., the removal of about 60% of the adsorbed nitrate followed by complete mixing of the bed and high-nitrate leakage exhaustion) was considerably more efficient than complete regeneration. For the production of 1.0 mgd (3,800 m^3/day) of 7.0 mg/L nitrate-N product water, partial regeneration consumes 890 lb/day (404 kg/day) less salt and produces a more concentrated wastewater with much less volume.

Complete mixing of partially regenerated beds is required to prevent excessive nitrate leakage on subsequent exhaustion. This was verified by mathematical modeling to predict the expected nitrate breakthrough curves from partially regenerated beds (typically 80% chloride and 20% nitrate) which indicated that excessive nitrate leakage should not occur in properly mixed beds. This predicted result was verified in laboratory column experiments in which the partially regenerated resins were removed from the columns, completely mixed and repacked in the columns prior to the next exhaustion which produced the expected, low-nitrate leakage.

The reuse of spent regenerant was attempted, as was counterflow (upflow) regeneration. These measures were ineffective but worthy of further study.

Upflow partial regeneration with 0.5 N NaCl was quite ineffective in removing nitrate from the spent resin following downflow exhaustion. This observation is not in agreement with previous studies by Gauntlett [9], in which counterflow partial regeneration was used, but in a different sequence (i.e., downflow regeneration following upflow exhaustion). In our study, uneven flow distribution during the upflow regeneration is suspected to have caused the poor results. Such uneven flow distribution during a similar upflow NaCl regeneration following chromate removal was clearly seen in a subsequent study in Scottsdale, Arizona.

During the course of this study, it was discovered that a measurable pH change resulting from carbonate elution accompanies and therefore signals nitrate breakthrough from completely regenerated beds. This phenomenon needs further study as a function of (1) the nitrate/sulfate selectivity of the resin, (2) the bicarbonate and sulfate concentration of the water, and (3) the partially regenerated condition of the bed.

The recommended method of treatment for 1.0 mgd (3800 m^3/day) of the Glendale water is chloride ion exchange followed by partial regeneration. This presumes that disposal can be arranged for 11,000 gal/day (42m^3/day) of spent regenerant containing 30,000 mg/L TDS and 5200 mg/L nitrate-N.

SECTION 3

RECOMMENDATIONS

Laboratory and pilot-scale studies should be carried out using the recently developed [7], nitrate-selective, styrene-DVB strong-base anion resins based on greater charge separation distance to reduce the sulfate preference and greater hydrophobicity to increase the nitrate affinity [3]. Resins that have, for example, triethyl, tripropyl, or tributyl quaternary functionality prefer nitrate to sulfate in dilute solution and will therefore avoid the nitrate peak that accompanies nitrate breakthrough when using the standard type 1 and type 2 resins. These new resins may also give somewhat longer runs and will be no more difficult to regenerate.

Further research and development should be carried out on regeneration efficiency, spent regenerant disposal, and nitrate breakthrough detection--the key issues in nitrate removal by chloride ion exchange, an effective and relatively inexpensive process.

Partial regeneration should be further studied on a laboratory scale using background waters containing various levels of sulfate, bicarbonate, and chloride. The effects of sulfate concentration on NaCl efficiency and pH detection of nitrate breakthrough should be examined in these tests using conventional and nitrate-selective resins. A mathematical model based on multicomponent chromatography theory and the laboratory results should be developed and tested in pilot studies.

To improve further the efficiency of partial regeneration, the following possibilities should be examined in pilot studies.

(a) Counterflow partial regeneration using upflow exhaustion and downflow regeneration.

(b) Reuse of spent regenerants for a roughing regeneration preceding a partial regeneration with fresh NaCL.

(c) Gradient elution using dilute to concentrated NaCl, or pulsed regeneration using a sequence of salt, water, and salt and water.

(d) Nitrate removal from a reusable regenerant using biological denitrification or porous nitrate-selective RO membranes.

(e) Sulfate elution of adsorbed nitrate in waters of high-sulfate content (i.e., deliberate elution of the nitrate peak while wasting the product water). This would be followed by a 1.0 N NaCl partial regeneration of the easy-to-remove sulfate.

Alternative regenerants such as $CaCl_2$ (dilute to avoid $CaSO_4$ precipitation) should be studied on a laboratory scale. The resulting calcium solutions of nitrate, sulfate, and chloride would be more amenable to land disposal than the current sodium solutions.

The development of alternative nitrate removal processes should continue to be followed carefully. These include:

(a) The CARIX partial demineralization process using CO_2 as a regenerant and producing a land-disposable wastewater [12].

(b) The Sirotherm partial demineralization process using heat as a regenerant [13].

(c) Above-ground, biological denitrification before distribution or groundwater recharge [14,15].

(d) Underground biological denitrification [16].

(e) Wetland denitrification in marshes.

SECTION 4

EXPERIMENTAL DETAILS

ANALYTICAL METHODS

Table 1 lists all analytical methods used in the experimental work. "Standard Methods of Water and Wastewater Analysis" [17] was followed for most analyses. An exception to this general practice was the use of a Hach Kit colorimetric method rather than the standard brucine method for nitrate analysis. This method is described in detail in Appendix E. The brucine method with its requirement for 95°C heating in H_2SO_4 solution was found to be both imprecise and inaccurate in this field application. Use of the low range nitrate Hach Kit was based on the recommendation of Guter [7] who also found it to be of acceptable precision and accuracy.

RAW WATER ANALYSIS

Table 2 presents the complete analysis of raw water from Glendale, Arizona well No. 1. Nitrate concentration is 19.2 mg/L as N, and total dissolved solids concentration is 532 mg/L. It represents a single sample taken during the first week of the study. Later it was found that the NO_3-N concentration varied from 18.3 to 25.5 mg/L during the 15-month study.

COLUMN STUDIES

All ion exchange exhaustion and regeneration column runs done in the field were performed using Glendale Well Number 1 water or regenerant solution fed to pilot sized columns containing 22.5 L (0.79 ft^3) or 47.0 L (1.67 ft^3) of anion resin. Some ion exchange column runs involving partial regeneration were performed at the University of Houston. These were done using synthetic Glendale, AZ water fed to 5.33 mm I.D. minicolumns containing 5.0 mL of resin and a typical empty bed contact time (EBCT) of five minutes.

TABLE 1
ANALYTICAL METHODS

Test	Method/Reference
Nitrate/Nitrogen (NO_3^-/N)	Colorimetric (Hach Kit, Cd Redn.)
Total Dissolved Solid (TDS)	Evaporation and weighing
Chloride (Cl^-)	Potentiometric Titration, $AgNO_3$
Magnesium (Mg^{2+})	Calculation (TH - CaH)
Silt Density Index (SDI)	DuPont RO Manual
Conductivity	HACH Conductivity Meter, Model 16300
Alkalinity	HACH Digital Titrator
Calcium (Ca^{2+})	EDTA Titrimetric
pH	HACH pH meter, Model 16400
Silica (SiO_2)	Molybdosilicate
Fluoride (F^-)	Electrode, Orion
Bicarbonate (HCO_3^-)	Titration with H_2SO_4
Sulfate (SO_4^{2-})	Turbidimetric, $BaCl_2$ ppt
Turbidity	HACH Turbidimeter, Model 2100 A
Total hardness (TH)	EDTA Titrimetric
Total Suspended Solid (TSS)	Filtration and weighing

TABLE 2
RAW WATER ANALYSIS FOR WELL NO. 1
GLENDALE, ARIZONA

Contaminant Concentration	Concentration mg/L	Concentration meq/L
pH	8.0	
Conductivity (microSiemens)	820.0	
Silt Density Index (SDI)	5.6	
Total Dissolved Solids	532.0	
Silica (SiO_2)	23.1	
ANIONS		
Total Alk ($CaCO_3$)	102.0	
NO_3^--N	19.2	1.37
F^-	0.52	0.03
Cl^-	122.5	3.45
$SO_4^=$	42.5	0.89
HCO_3^-	124.0	2.03
	meq anions	7.77
CATIONS		
Total Hardness ($CaCO_3$)	198.0	
Ca^{++}	43.0	2.15
Mg^{++}	28.0	2.30
Na^+ (by difference)	76.0	3.30
Fe^{++}	0.26	0.01
	meq cations	7.76

RESEARCH OUTLINE

The following experiments were run. Results and discussion are presented in the next section of this report.

I. Electrodialysis, determine % removal of all ions

  Run No. EDR-1

II. Reverse osmosis, compare % removals for 2 membranes

  A. DuPont aramid membrane--Run No. RO-1
  B. Dow cellulose triacetate membrane-- Run No. RO-2

III. Ion Exchange, evaluate exhaustion and regeneration

  A. Comparison of three resins

    1. ASB 1--Run No. 1
    2. ASB 2--Run Nos. 2, 3
    3. DOWEX 11--Run No. 4

  B. Effect of sulfate concentration

    1. 140 ppm--Run No. 5
    2. 310 ppm--Run No. 6

  C. Effect of regenerant NaCl concentration--complete regeneration

    1. 0.25 N--Run Nos. 23, 24
    2. 0.5 N--Run No. 7
    3. 1.0 N--Run No. 8
    4. 2.0 N--Run Nos. 2, 3, 10
    5. 3.0 N--Run No. 9

  D. Reuse of spent regenerant

    1. 2.0 N--Run Nos. 10, 11
    2. 0.5 N--Run Nos. 12, 13, 14, 15

  E. Partial regeneration

    1. 1 eq salt/eq resin
      a. 1.0 N NaCl--Run Nos. 16, 17
      b. 0.5 N NaCl--Run Nos. 19, 20
      c. 0.25 N NaCl--Run Nos. 25, 26
    2. 0.64 eq salt/eq resin
      a. 1.0 N NaCl--Run No. 18
    3. 2 eq salt/eq resin
      a. 1.0 N NaCl--Run Nos. 27, 28
    4. upflow--Run Nos. 21, 22

5. high sulfate--Run Nos. 29, 30

F. Laboratory evaluations at UH

1. selectivity reversal studies
2. partial regeneration studies
3. resin mixing after regeneration

A chronological tabulation of exhaustion and regeneration runs is presented in Tables 6 and 11 in the Results and Discussion section. The experimental data for the EDR, RO and IX runs have been plotted in Appendices A, B and C respectively.

SECTION 5

RESULTS AND DISCUSSION

PERFORMANCE OF THE EDR UNIT

Run No. EDR-1 (Figure A-1) shows the effluent concentration histories observed during 80 hours of EDR treatment of Glendale, Arizona, well water for nitrate removal. Nitrate removal averaged 96%, sulfate 97%, bicarbonate 93%, and chloride 88%. The data are summarized in Table 3. As expected for non-ionic species, silica was not removed by the EDR unit. Product water recovery was 76% of feed. During this run, there was no pretreatment except the protective cartridge filter and the activated carbon filter. The carbon was actually unnecessary since the raw water contained no chlorine.

TABLE 3
GLENDALE, ARIZONA
EDR RESULTS

Ion	Feed mg/L	Product mg/L	Brine mg/L	% Removal
NO_3-N	19.2	0.8	67.5	96
Cl^-	122.5	15.0	465	88
HCO_3^-	129	9.0	500	93
SO_4^{2-}	43.7	1.5	171	97
pH	8.0	5.9		

$$\text{Average Recovery} = \frac{Q_P}{Q_F} = 76\%$$

PERFORMANCE OF THE RO UNIT WITH DUPONT MODULE

The DuPont RO module was operated to achieve desalting and nitrate removal from a 19.2 mg/L nitrate, 530 mg/L TDS feedwater in Glendale, Arizona. The feedwater pH was adjusted to 6.8 with H_2SO_4; 10 mg/L SHMP was added for scale control. However, the feedwater pH control failed after the first 40 hours of this run because the acid metering pump was broken. During the 100-hour run, the average percent product recovery was 46%. Nitrate removal averaged 94%, sulfate 98%, bicarbonate 95%, and chloride 95% as listed in Table 4. Run No. RO-1 (Figure B-1) shows the effluent histories resulting from the operation of the RO Unit with the DuPont module.

TABLE 4
GLENDALE, ARIZONA
RO RESULTS
DUPONT (HOLLOW FIBER MEMBRANE)

Ion	Feed mg/L	Product mg/L	Reject mg/L	% Removal
NO_3-N	18.2	1.2	32	94
Cl^-	125	6.0	234	95
HCO_3^-	129	6.0	230	95
SO_4^{2-}	43	<1.0	76	98
pH	8.1			

$$\text{Average Recovery} = \frac{Q_P}{Q_F} = 46\%$$

Failure of pH control did not adversely affect RO operation. It is desirable to maintain pH in the low neutral range to prevent precipitation of calcium carbonate scale. In this case, the raw water pH was 8.1, which is more than 2 pH units below the pKa of bicarbonate. Therefore, even without acid addition, bicarbonate was the predominant species and carbonate concentration remained too low to cause a scale problem.

PERFORMANCE OF THE RO UNIT WITH DOW MODULE

The Dow RO module was operated to achieve desalting and nitrate removal from a 19.2 mg/L, 523 mg/L TDS feedwater in Glendale, Arizona. The total dissolved solids were 88 mg/L in the product stream and 2597 mg/L in the reject stream. The feedwater pH was adjusted to 6.7 with

H_2SO_4; 10 mg/L SHMP was added for scale control. During the 100 hour run, the average % product recovery was 75%, while the overall dissolved solids rejection was 86% and nitrate removal averaged 76%. These results are listed in Table 5. Run No. RO-2 (Figure B-2) shows the effluent histories resulting from the operation of the RO unit with Dow module.

TABLE 5
GLENDALE, ARIZONA
RO RESULTS
DOW (CELLULOSE TRIACETATE MEMBRANE)

Ion	Feed mg/L	Product mg/L	Reject mg/L	% Removal
NO_3-N	19.2	4.6	60	76
HCO_3^-	80	5.1	262	94
SO_4^{2-}	80	2.7	340	97
TDS	618	88	2597	86
pH	8.1			

$$\text{Average Recovery} = \frac{Q_P}{Q_F} = 74\%$$

COMPARISON OF EDR AND RO PROCESSES

The polyamide RO membrane performed better than cellulose triacetate on the basis of nitrate rejection (94% compared with 76%), but ED, which produced 96% rejection at 76% recovery, performed better than either membrane. The results of this study indicate that overall, ED is slightly superior to RO when estimated costs, nitrate rejection, and degree of pretreatment are taken into consideration.

RESULTS OF ION EXCHANGE EXHAUSTION RUNS

Exhaustion Results Summary

Nineteen of the thirty ion exchange exhaustion runs were monitored for nitrate breakthrough with the results summarized in Table 6. The actual breakthrough curves are presented in the Appendix C Figures with numbers corresponding to the Run Numbers in Table 6.

TABLE 6
SUMMARY OF ION EXCHANGE EXHAUSTION RUNS

Run No.	BV to NO_3-N MCL	Comments
1	422	Type 1 (ASB-1) resin, C_0 = 18.6 ppm N
2	410	Type 2 (ASB-2) resin, C_0 = 21.5 ppm N
3	410	ASB-2, low flow rate, C_0 = 22 ppm N
4	345	Isoporous Type 1 (Dowex 11), C_0 = 25.5 ppm N
5	245	ASB-2, Feed $SO_4^=$ = 140 ppm
6	177	ASB-2, Feed $SO_4^=$ = 310 ppm
7-16	Exhaustion only for complete regeneration studies	
17	346	Partial (1/1) regen., leakage = 11 ppm N
18	323	Partial (1/1) regen., leakage = 15 ppm N
19	320	Partial (0.64/1) regen., leakage > 25 ppm N
20	338	Partial (1/1) regen., leakage = 15 ppm N
21	322	Partial (1/1) regen., leakage = 16 ppm N
22	30	Upflow partial regeneration failed
23	0	Upflow partial regeneration failed
24	420	Complete regeneration, 0.25 N
25	410	Complete regeneration, 0.25 N
26	330	Partial (1/1) regen., leakage = 17 ppm N
27	340	Partial (1/1) regen., leakage = 16 ppm N

Notes: C_0 = conc., of NO_3-N in feedwater; ppm N = ppm NO_3-N.
Partial (1/1) regen. = partial regeneration with 1 equiv. Cl^-/equiv. resin.
Leakage values are NO_3-N concentrations at approximately 10 BV after start of run.

TABLE 6 (continued)

Run No.	BV to NO_3-N MCL	Comments
28	370	Partial (2/1) regen., leakage = 12 ppm N
30	115	Partial (1/1) regen., Feed $SO_4^=$ = 404 ppm

Notes: C_0 = conc., of NO_3-N in feedwater; ppm N = ppm NO_3-N.
Partial (1/1) regen. = partial regeneration with 1 equiv. Cl^-/ equiv. resin.
Leakage values are NO_3-N concentrations at approximately 10 BV after start of run.

During the resin exhaustion studies, the effects of resin type, empty bed contact time (EBCT), sulfate concentration, level of regeneration and direction of regeneration were evaluated. The flow rate and resin type made little difference in the process performance. However, the differences between complete and partial regenerations were substantial. A completely regenerated bed of ASB-2 resin could be expected to run for 400 BV before the NO_3-N MCL was reached. The partially regenerated beds always exhibited excessive initial leakage and shorter runs, typically 330 BV, to the nitrate MCL.

When the feedwater was spiked with sulfate, the additional sulfate severely reduced the nitrate capacity of the resin as expected. This was true for both partially and completely regenerated beds. A detailed analysis of these effects of the nitrate breakthrough curves and nitrate capacities follows.

Finally, it was observed that the nitrate capacity of the resin used for most of the runs did not decrease measurably upon repeated regeneration (28 cycles). This good performance may be expected for any typical styrene-divinylbenzene strong base anion resin used on the Glendale water.

Effect of Resin Type

From Clifford and Weber's list of commercially available strong base anion exchange resins acceptable for nitrate removal from sulfate and chloride-containing water, three were chosen for initial evaluation. These were Ionac ASB-1, Ionac ASB-2, and Dowex-11. All are styrene-divinylbenzene based resins, but they differ in functionality, porosity, capacity and selectivity coefficient. The relevant characteristics of these three resins are presented in Table 7. All were expected to be suitable for the required separation, but it was desired to verify the Clifford-Weber recommendations for a few resins in field tests before choosing a single type for all further Glendale studies.

TABLE 7
ANION RESIN CHARACTERISTICS

Manufacturer's Designation	Ionac ASB-1	Ionac ASB-2	Dowex-11
Matrix	STY-DVB	STY-DVB	STY-DVB
Functionality	Q-1	Q-2	Q-1
Porosity	MICRO	MICRO	ISO
Meq/mL Advertised Capacity	1.40	1.52	1.20
Meq/mL Measured HCl Capacity	1.39	1.33	1.17
pKa	>13	>13	>13
Average alpha S/N	1.87	3.04	3.37
Average alpha N/Cl	3.0	3.64	3.0

Q-1 = Quaternary Amine - Type 1
Q-2 = Quaternary Amine - Type 2
ISO = Isoporosity or "Improved Porosity"

Column tests were run to determine the nitrate breakthrough curve for each resin after complete regeneration with 2.0 N NaCl. These curves are presented for Run Nos. 1 through 4 in Appendix C. Bed volumes to nitrate breakthrough, (BV(N)), and the fraction nitrate in the exhausted resin, (y_N), for each test run are listed in Table 8. As expected, there is no significant difference in performance for the three resin types.

Although any of these three resins would be acceptable for nitrate removal, ASB-2 was chosen for further study on the basis of slightly higher y_N and nitrate/chloride selectivity.

Effect of Flow Rate

Sharp chromatographic separation of ions on an ion exchange column requires that the resin and liquid phases be at equilibrium everywhere in

TABLE 8
COMPARISON OF RESIN PERFORMANCE

Resin Type	ASB-1	ASB-2	ASB-2	DOWEX-11
Run No.	1	2	3	4
Bed Volumes	47	47	24.3	24.3
BV to NO_3^- Breakthrough (10 ppm) after 2 N salt Complete Regeneration, BV_N	414	404	406	346
meq/mL measured HCl Capacity	1.39	1.33	1.33	1.17
Fraction NO_3^- in Exhausted Resin, Y_N	0.403	0.416	0.418	0.405
Throughput = $\frac{\text{Equiv. Feed Ions}}{\text{Equiv. Resin Cap.}}$	2.39	2.43	2.43	2.27

the column at all times. If the flow rate of liquid through the bed is too fast, fluid-resin contact time is too short and equilibrium is not established.

The empty bed contact time (EBCT) is a residence time defined as follows:

$$\text{EBCT} = \frac{\text{Resin Bed Volume}}{\text{Volumetric Flow Rate}} = \frac{\text{L}}{\text{L/min}} = \text{min}$$

All ion exchange column exhaustion runs described in this report had EBCT greater than four minutes. Comparison of Runs 2 and 3 shows no significant effect of flow rate on nitrate breakthrough in the range from 4.05 to 9.44 min EBCT as shown in Table 9. This indicates that the sharpness of the breakthrough curves is not measurably improved by increasing the EBCT beyond 4.0 minutes. No attempt was made to determine the minimum EBCT.

Effect of Sulfate Concentration on Nitrate Breakthrough

The nitrate breakthrough is dependent on the concentration of sulfate and other adsorbable ions in the feed water. Since sulfate is preferred by strong-base anion exchangers, increasing feed water sulfate concentration results in a shorter run length to nitrate breakthrough and a smaller fraction of nitrate on the exhausted resin at breakthrough. Thus, the efficiency of the ion exchange process for nitrate removal is reduced by competition with sulfate.

TABLE 9
EFFECT OF EBCT ON NITRATE BREAKTHROUGH

Run No.	Resin Type	EBCT	Bed Volumes to NO_3^- Breakthrough
2	ASB-2	9.44 min	406
3	ASB-2	4.05 min	404

The natural sulfate concentration of Glendale well water is 42.5 mg/L. To test the effect of increased sulfate concentration, Glendale water was spiked with Na_2SO_4 to adjust sulfate concentration to 140 mg/L and 310 mg/L for experimental Runs 5 and 6, respectively. Note that in Run 6, sulfate breaks through before nitrate, i.e. the selectivity is reversed due to high ionic strength. The results are listed in Table 10 and plotted in Figure 4. The actual nitrate and sulfate breakthrough curves are plotted in chronological order in Appendix C where the figure number and the exhaustion run number are identical.

TABLE 10
EFFECT OF SULFATE CONCENTRATION ON THE PERFORMANCE OF ASB-2 RESIN

$SO_4^=$ conc. mg/L	Run No.	NO_3^- Breakthrough BV	$SO_4^=$ Breakthrough BV
42.5	2	400	>750
140	5	240	290
310	6	180	160

RESULTS OF THE REGENERATION STUDIES

Regeneration Data Summary

Using primarily a quaternary type-2 resin (ASB-2) several different methods of regeneration were studied in detail by exhausting and

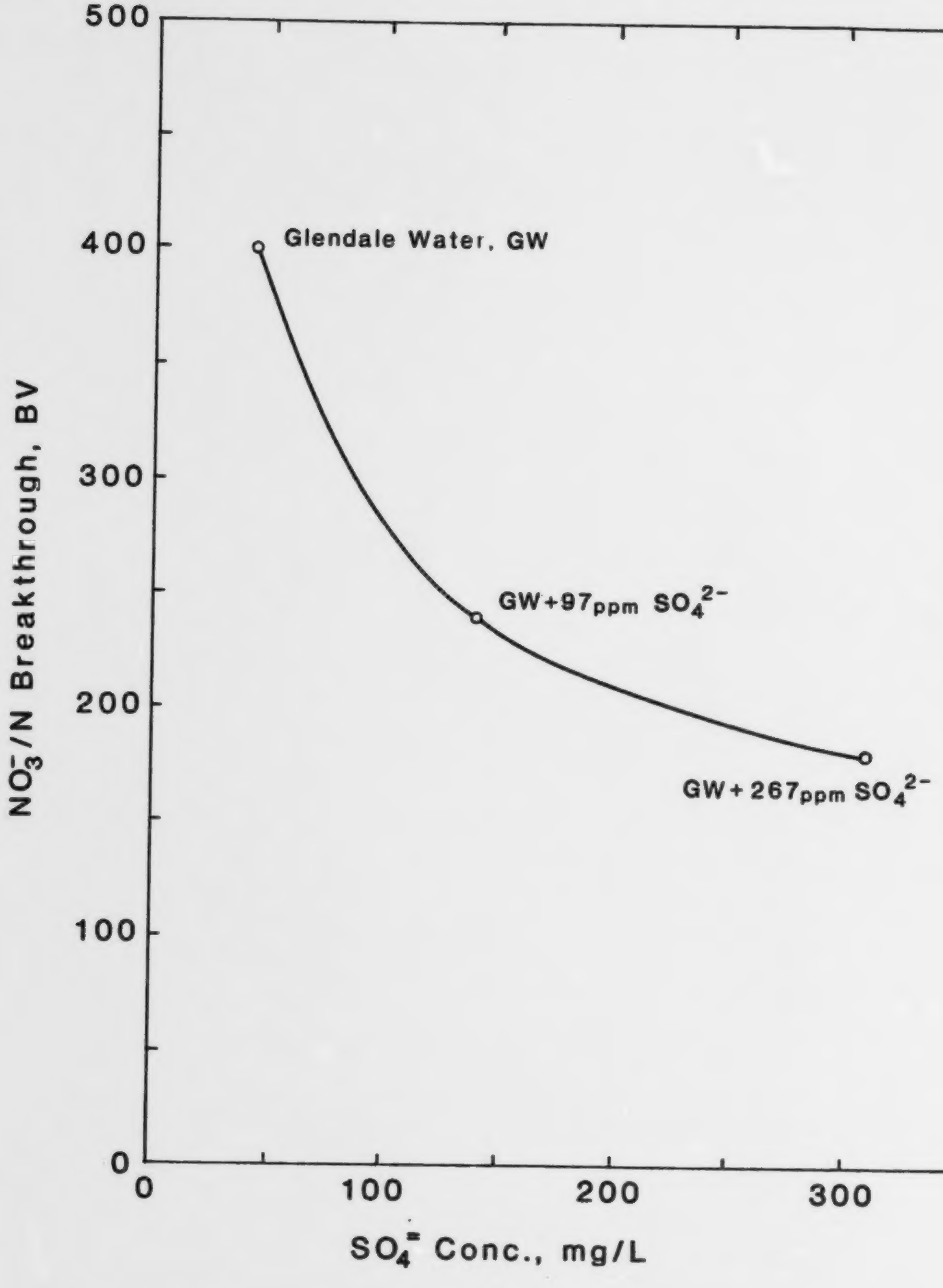


Figure 4. Effect of sulfate concentration on nitrate breakthrough using raw and sulfate spiked Glendale water.

regenerating the pilot columns thirty times. The efficiency of each regeneration was calculated in terms of the gram equivalents of chloride required to remove a gram equivalent of nitrate from the raw water or spent resin. These efficiencies are presented in Table 11 which summarizes the data from all the regenerations in chronological order. The specific method of regeneration studied were (1) complete, regeneration, (2) reuse of spent regenerant followed by a polishing regeneration and (3) partial (or incomplete) regeneration. Various NaCl concentrations between 0.25 and 3.0 N were utilized for the regenerations. Twenty-eight of the thirty regenerations were downflow i.e. cocurrent, while only two were upflow (countercurrent) because the latter was clearly on inferior method, at least with our simple column design.

TABLE 11
SUMMARY OF ION EXCHANGE REGENERATION RUNS

Run No.	Resin Type	Condition	$\frac{\text{eq. Cl}^-}{\text{eq Resin}}$	$\frac{\text{eq. Cl}^-}{\text{eq N,feed}}$	$\frac{\text{eq. Cl}^-}{\text{eq N,Resin}}$	Comments
1R	ASB-1	2 N Complete	6.2	15.6		NO_3^-Cap.=7680g/m^3
2R	ASB-2	2 N Complete	7.2		18.2	NO_3^- Cap.=8287 g/m^3
3R	ASB-2	2 N Complete	8.8	18.1		NO_3^- Cap.=8733 g/m^3 Insufficient Regen.
4R	DOWEX 11	2 N Complete	-	-	-	NO_3^- Cap.=8893 g/m^3
5R	ASB-2	2 N Complete	6.2		27.8	$C_{SO4^=}$,feed= 140 ppm
6R	ASB-2	2 N Complete	6.5		36.0	$C_{SO4^=}$,feed=310 ppm
7R	ASB-2	0.5 N Complete	3.5		10.9	
8R	ASB-2	1 N Complete	5.2		18.6	
9R	ASB-2	3 N Complete	8.7		22.6	

TABLE 11 (continued)

Run No.	Resin Type	Condition	$\frac{\text{eq. Cl}^-}{\text{eq Resin}}$	$\frac{\text{eq. Cl}^-}{\text{eq N,feed}}$	$\frac{\text{eq. Cl}^-}{\text{eq N,Resin}}$	Comments
10R	ASB-2	2 N Complete	6.7		18.9	Collect spent for Regenerant 11
11RS	ASB-2	2 N Spent	6.0	15.0		
11R2	ASB-2	2 N Complete				Polishing Regen.
12R	ASB-2	0.5 N Complete	4.1		11.5	Collect spent for Regenerant 13
13RS	ASB-2	0.5 N Spent	3.9	9.6		Collect spent for Regenerant 14
13R2	ASB-2	0.5 N Complete				Polishing Regen.
14RS	ASB-2	0.5 N Spent	4.0	10.0		Collect spent for Regenerant 15
14R2	ASB-2	0.5 N Complete				Polishing Regen.
15RS	ASB-2	0.5 N Spent	3.5	8.6		
15R2	ASB-2	0.5 N Complete				Polishing Regen.
16RP	ASB-2	1 N Partial	1.0	4.63		
17RP	ASB-2	1 N Partial	1.0	5.87		Repeat Run 16
18RP	ASB-2	1 N Partial	0.64	6.79		
19RP	ASB-2	0.5 N Partial	1.0	5.57		

TABLE 11 (continued)

Run No.	Resin Type	Condition	$\frac{\text{eq. Cl}^-}{\text{eq Resin}}$	$\frac{\text{eq. Cl}^-}{\text{eq N,feed}}$	$\frac{\text{eq. Cl}^-}{\text{eq N,Resin}}$	Comments
20RP	ASB-2	0.5 N Partial	1.0	5.63		Repeat Run 19
21RPU	ASB-2	.5N Upflow Partial	1.0	x		effluent NO_3-N > 10 ppm, Run 22
22RPU	ASB-2	.5N Upflow Partial	1.0	x		Repeat Run 21 effluent NO_3-N > 10 ppm, Run 23
23R	ASB-2	0.25N Complete	2.9		6.9	
24R	ASB-2	0.25N Complete	2.7		7.4	Repeat Run 23
25RP	ASB-2	0.25N Partial	1.0	5.94		
26RP	ASB-2	0.25N Partial	1.0	6.06		Repeat Run 25
27RP	ASB-2	1 N Partial	2.0	6.81		
28RP	ASB-2	1 N Partial	2.0			Repeat Run 27
29RP	ASB-2	1 N Partial	1.0	24.46		$C_{SO_4^=}$,feed=310 ppm Run 29
30RP	ASB-2	1 N Partial	1.0			$C_{SO_4^=}$,feed=404 ppm Run 30

Note: eq. Cl^-/eq. Resin = equivalent of chloride regenerant applied per equivalent of resin sites.

eq. Cl^-/eq. N, Feed = equivalents of chloride regenerant applied per equivalent of NO_3-N removed from the feed.

eq. Cl^-/eq. N, Resin = equivalents of chloride regenerant applied per equivalent of NO_3-N removed from the spent resin.

In all the above ratios the salt requirement for complete regeneration is based on approx. 95% removal of nitrate from the resin.

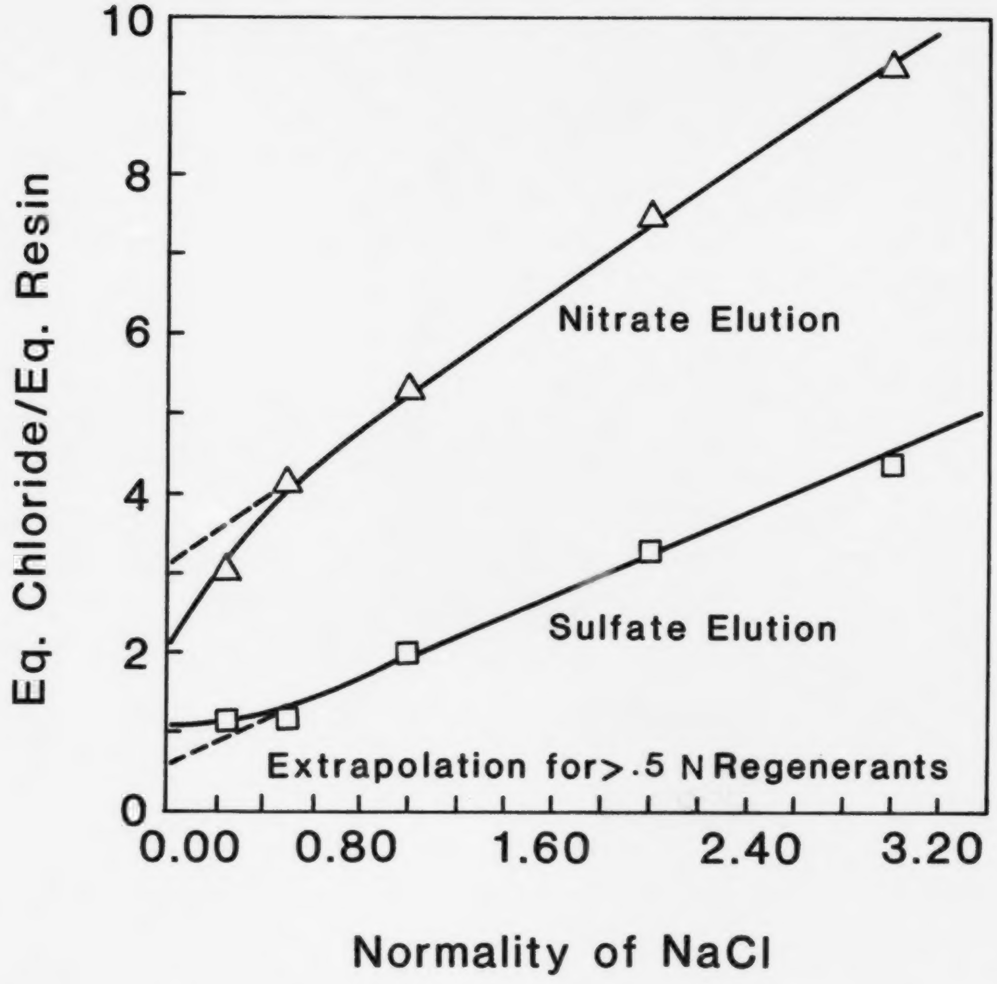


Figure 5. Inefficiency of nitrate and sulfate elution from exhausted ASB-2 resin as a function of regenerant concentration.

Regardless of the regeneration method used, sulfate was much easier to strip from the spent resin than was nitrate. This can readily be seen in all the regeneration elution curves, Figures C-1R through C-30RP, in Appendix C where the Figure numbers are the same as the run numbers. The figures are presented in chronological order. The number is the exhaustion Run No. and suffixes are as follows:

R = complete regeneration.
RP = partial regeneration.
RPU = upflow partial regeneration.
RS = regeneration with spent regenerant containing nitrate and sulfate.
R2 = polishing regeneration following a spent regeneration i.e. the second regeneration following the indicated exhaustion run.

In determining the efficiencies of regeneration, the chloride required for nitrate elution during a complete regeneration was determined from the regenerant concentration and the number of BV's required to elute approximately 95% of the nitrate as measured by the area under the elution curve. Generally, a regeneration was "complete" when the NO_3-N concentration in the eluate fell to within the 100-200 mg/L range.

Complete Regenerations

Efficiency of sulfate and nitrate elution--

The ease of sulfate compared to nitrate elution as a function of regenerant NaCl concentration is presented in Figure 5 which is based on the data in Tables 12 and 13. Although sulfate is considerably easier to elute than nitrate, the elution of both anions becomes much less efficient as the regenerant NaCl concentration is increased. For example, when using 0.5 N NaCl (3%), a total of 4.1 chloride ions per resin site are required to elute the nitrate whereas only 1.2 chloride ions per resin site are needed to elute the sulfate. When the NaCl concentration is increased to 3.0 N, sulfate elution requires 4.4 chloride ions per site while nitrate elution requires 9.4 chloride ions per resin site.

Sulfate is the first to be stripped from the resin during regeneration because of the selectivity reversal phenomenon which takes place with polyvalent ions in concentrated regenerant solutions. Divalent ions like sulfate (and calcium in cation exchange) are highly preferred over monovalent ions like nitrate by the concentrated resin phase (typically > 1.00 N) when the resins are in equilibrium with natural waters of low ionic concentration (typically < 0.010 N). During regeneration, the ionic concentration difference between the phases tends to disappear with the result that polyvalent ions are now preferred by the aqueous phase. This reversal in preference does not take place with monovalent ions like nitrate and chloride. The electroselectivity reversal phenomenon is graphically depicted in Figures 6 and 7. In Figure

6 the binary, divalent/monovalent (sulfate/nitrate) exchange reverses to favor monovalent nitrate as the aqueous phase concentration increases from 0.005 N to 0.500 N. This selectivity reversal is absent in binary monovalent/monovalent nitrate/chloride exchange (Figure 7) as the aqueous phase concentration increases in the same range.

TABLE 12
EFFICIENCY OF SULFATE ELUTION FROM ASB-2 RESIN

Regeneration Runs	NaCl N	EBCT min.	Elute SO_4^{2-} BV	$\frac{\text{Eq. } Cl^-}{\text{Eq. Resin}}$
9	3.0	18.1	1.9	4.4
2,3,5,6,10	2.0	15.7	2.2	3.3
8,27,28	1.0	11.9	2.7	2.0
7,12	0.5	12.0	3.1	1.2
23,24	0.25	12.5	5.9	1.1

Notes: All values are averages for the runs indicated. Values are for approximately 95% elution of sulfate

TABLE 13
EFFICIENCY OF NITRATE ELUTION FROM ASB-2 RESIN

Regeneration Runs	NaCl N	EBCT min.	Elute NO_3^- BV	$\frac{\text{Eq. Cl}}{\text{Eq. Resin}}$
9	3.0	18.1	4.1	9.4
2,3,10	2.0	17.2	5.0	7.5
8	1.0	11.3	7.1	5.3
7,12	0.5	12.0	11.0	4.1
23,24	0.25	12.5	16.0	3.0

Notes: All values are averages for the runs indicated. Values are for elution of approximately 95% of nitrate on column.

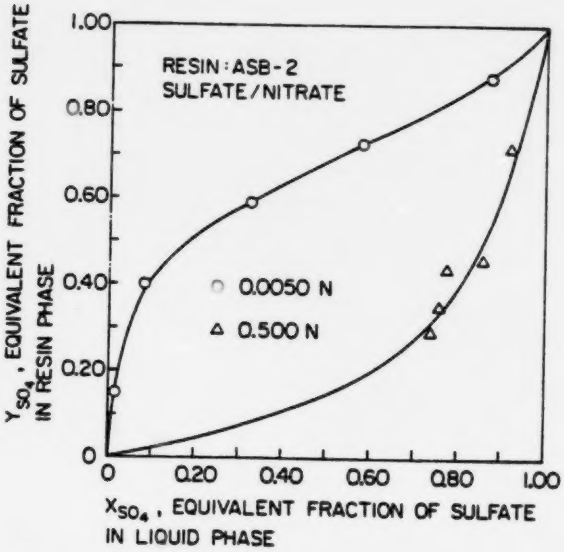


FIGURE 6. Binary sulfate/nitrate ion exchange isotherms showing selectivity reversal between dilute and concentrated solutions for a quaternary, type 2 resin.

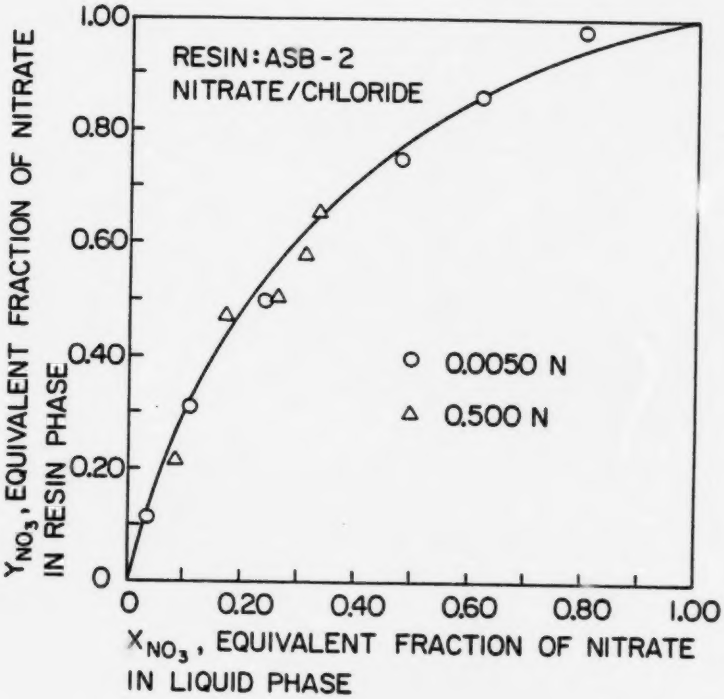
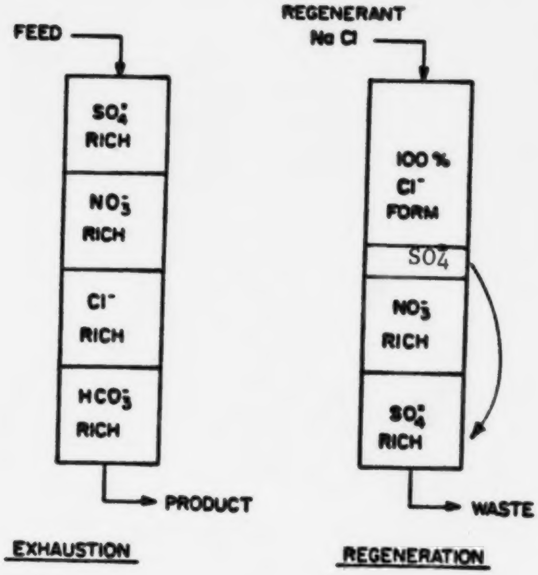


FIGURE 7. Binary ion exchange isotherm for monovalent/monovalent exchange in dulute and concentrated solutions for a quaternary, type 2 resin.

The movement of sulfate, nitrate chloride and bicarbonate zones through the column during exhaustion and regeneration are shown schematically in Figure 8. Here it may be seen that during exhaustion the most preferred sulfate is concentrated near the column inlet but upon regeneration it bypasses the harder-to-remove nitrate.



$$\overline{R\text{-}Cl} + NO_3^- \rightleftharpoons \overline{R\text{-}NO_3} + Cl^-$$

FIGURE 8. Exhaustion and regeneration steps in the chloride-form ion exchange process for nitrate removal. Sulfate bypasses nitrate during cocurrent regeneration.

By extrapolation to infinitely dilute regenerant solution in Figure 5, it is evident that sulfate may be completely eluted with approximately one chloride ion per resin site while nitrate elution would require a minimum of two chloride ions per site. Care must be exercised, however, in applying these extrapolated results to other resins and to feedwaters of composition different than Glendale's Well No. 1. Nevertheless, it can generally be stated, regardless of resin or feedwater, that nitrate will be much more difficult to elute from a spent resin than sulfate. Anions resins may be designed to prefer nitrate to sulfate in dilute solution by separating the charged sites and making the resin phase more hydrophobic. However, these resins will elute sulfate even more easily than the conventional resins which we used, thus the regeneration problem will remain.

Comparison among complete regeneration conditions--

Although dilute regenerants more efficiently use chloride to elute nitrate they yield greater wastewater volume, and increase the required regeneration time, these trade-off relationships are presented in Table 14 where calculated values of salt consumed per 1000 gallons of blended (7 ppm NO_3-N) product water are listed. It is evident that, based on salt consumption alone, the most dilute regenerants are to be preferred. However, in those situations where it is important to minimize the wastewater volume, more concentrated regenerants may be preferred. The relationships among salt consumption, wastewater volume and regenerant NaCl concentration are depicted in Figure 9. The wastewater volume (spent regenerant plus 2 BV of slow rinse) rises sharply as regenerant concentration falls below 1.0 N NaCl (6.0%). Regenerant concentrations in the range of 0.25-1.0 N are recommended with the choice of exact NaCl concentration depending on the cost of NaCl vs. the cost of regenerant disposal.

TABLE 14
COMPARISON OF POSSIBLE COMPLETE REGENERATION CONDITIONS

NaCl N	Stoich. Ratio	NaCl BV	EBCT min.	Time hr.	$\frac{\text{lb NaCl}}{\text{1000 gal}}$	$\frac{\text{g NaCl}}{m^3}$
3.0	9.4	4.1	20	2.0	10.0	1200
2.0	7.5	5.0	18	2.1	8.13	980
1.0	5.3	7.1	15	2.3	5.77	692
0.5	4.1	11.0	12	2.6	4.47	536
0.25	3.0	16.0	10	3.0	3.25	390

Notes: Stoich. ratio is the eq. Cl^-/eq resin required for elution of 95% of the nitrate. Time is the regeneration time including 2 BV displacement rinse. NaCl requirements are based on 21 ppm NO_3-N feed, 7 ppm NO_3-N in blended product water, 33% bypass flow, and a run length of 400 BV before regeneration.

The compositions and volumes of the regenerant wastewater solutions as a function of concentration are given in Table 15. Because of the increasing efficiency of NaCl consumption as regenerant concentration is reduced, the regenerant wastewater volume only doubles (from 1.5% to 3.0%) as the regenerant concentration is quartered (from 1.0 N to 0.25 N). The TDS levels of the wastewater vary from 14,100 to 48,100 mg/L while the nitrate concentration (not NO_3-N) varies from 2060 to 4160

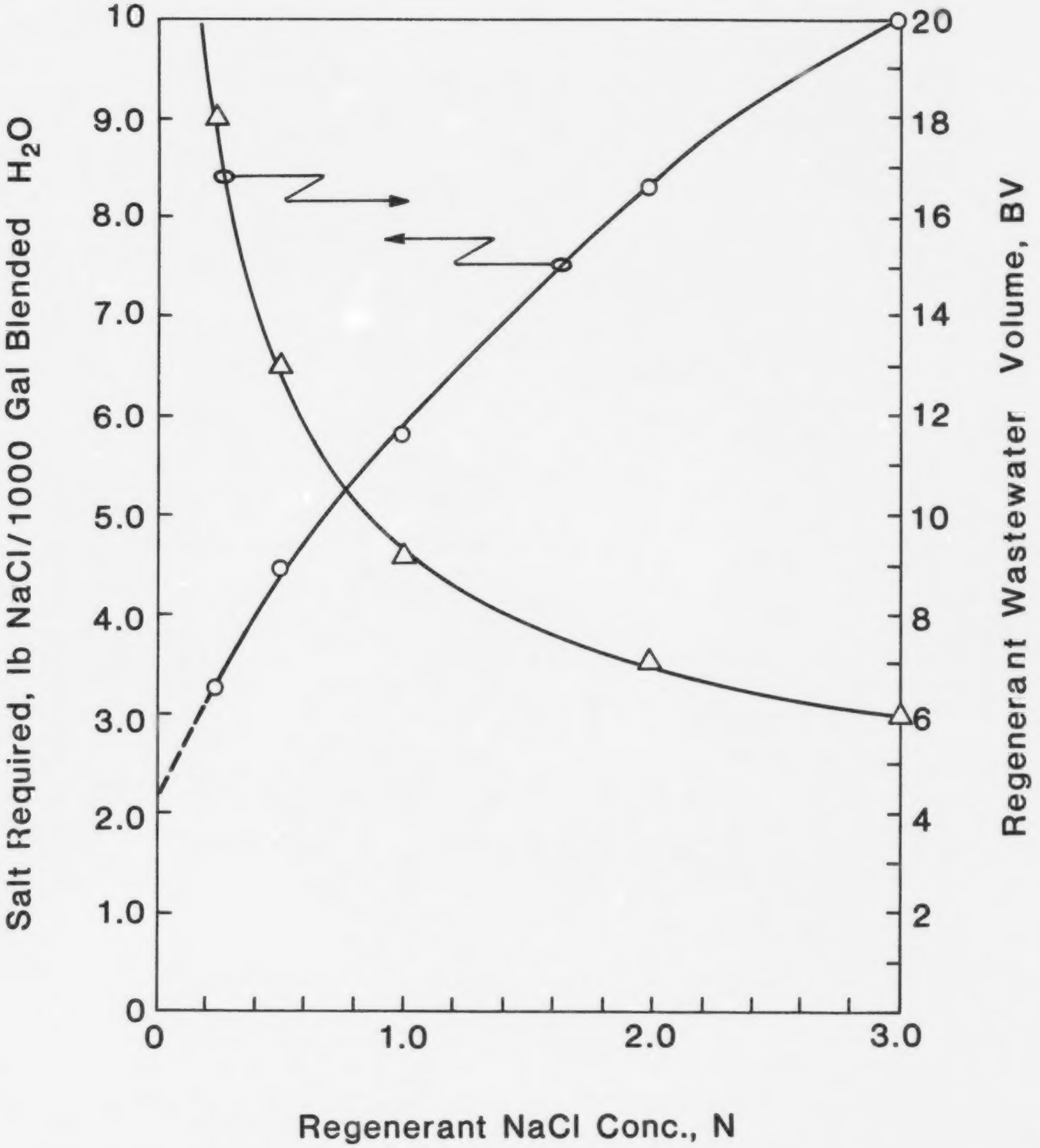


Figure 9. Comparison of salt consumption and amount of regenerant wastewater produced as a function of regenerant concentration.

mg/L. The disposal of such high-nitrate, high TDS solutions continues to be an unsolved problem in non-coastal, non-arid regions.

TABLE 15
CALCULATED COMPOSITION OF REGENERANT WASTEWATER SOLUTIONS

Description	Concentration of Regenerant NaCl 1.0 N	 0.5 N	 0.25 N
Regeneration time, hr	2.3	2.6	3.0
Regenerant NaCl vol., BV	7.1	11.0	16.0
Slow rinse vol., BV	2.0	2.0	2.0
Wastewater vol., BV	9.1	13.0	18.0
Wastewater vol. as a % of blended product water	1.5	2.2	3.0
Sodium conc., mg/L	18,000.	9,700.	5,110.
Chloride conc., mg/L	24,000.	12,400.	6,000.
Nitrate conc., mg/L	4,160.	2,900.	2,060.
Sulfate conc., mg/L	48,100.	26,300.	14,100.
NaCl consumption for 1.0 mgd blended product water, lbs/day	5,770.	4,470.	3,250.
kg/day	2,620.	2,030.	1,480.
Wastewater volume for 1.0 mgd blended product water, gal/day	15,000.	22,000.	30,000.
m^3/day	56.8	83.3	114.

Notes: Ions in raw water used to make up regenerant solution are not included. Nitrate is given as NO_3^-, not NO_3-N. NaCl requirements are based on 21 ppm NO_3-N feed, 7 ppm NO_3-N in blended product water, 33% bypass flow, and a run length of 400 BV before regeneration. Using 0.5 N solution saves 1300 lbs NaCl/day but produces an extra 7000 gal wastewater.

It is interesting to examine the NaCl efficiency vs. wastewater volume trade-off for a 1.0 MGD (blended product water with 33% bypass flow) plant treating Glendale water or water of similar nitrate and sulfate concentration. The comparison is also given in Table 15. Reducing the NaCl concentration to 0.25 N from 1.0 N saves 2,520 lbs NaCl/day while doubling the wastewater volume to 30,000 gal/day from 15,000 gal/day.

Reuse of Regenerant

Reuse of regenerant was tested as a means of increasing the NaCl regeneration efficiency of single-bed anion exchange for nitrate removal. The objective was to roughly regenerate the exhausted bed with the spent regenerant containing sulfate, nitrate and unused chloride from the previous regeneration. The second "polishing regeneration" using fresh NaCl would presumably require less NaCl than was used in the standard one-step complete regeneration. Obviously, the two-step, rough/fresh regeneration would have to be repeated several times to produce a relatively constant composition, spent-regenerant solution that would occur in an actual process at steady state.

It was found that, depending on the NaCl concentration of the original regenerant solution, the spent regenerant may or may not remove some nitrate from the exhausted resin. Table 16 shows the experimental results. Note that a relatively constant NO_3^- concentration in the spent regenerant was achieved after a single repetition.

TABLE 16
NITRATE REMOVAL DURING ROUGHING REGENERATION WITH SPENT REGENERANT

Original NaCl Conc., N	Regeneration Run No.	mg/L NO_3-N in Spent Regen.	% NO_3-N Removed
2.0	11RS	1400	0
0.5	13RS	608	29
0.5	14RS	300	47
0.5	15RS	330	50

Although substantial amounts (up to 50%) of nitrate are removed during the roughing regeneration with 0.5 N NaCl, the subsequent fresh regeneration is particularly inefficient because (a) there is no longer any sulfate on the resin, and (b) the nitrate has replaced the easy-to-remove sulfate at the bed inlet and is more uniformly distributed throughout the bed. These points are well illustrated by regeneration Run Numbers 11RS, 13RS, 14RS, and 15RS in Appendix C which show the amounts of sulfate and nitrate eluted during the roughing regenerations. The nitrate deposition near the top of the exhausted bed during regeneration with the spent regenerant containing 608 ppm NO_3-N may be inferred from Figure C-13RS. During sulfate elution, the nitrate concentration is below that in the influent spent regenerant. The sorbed nitrate along with a smaller amount of chloride is replacing the eluted sulfate. Unfortunately, this nitrate uptake is occuring at the inlet of the bed where it is more difficult to remove due to the fact that the pure chloride used during the polishing regeneration must drive this nitrate the entire length of the bed. This is different from the original exhausted bed in which very little nitrate is found near the bed inlet.

When the concentration of nitrate-N in the spent regenerant is very high, e.q. 1400 mg/L as in Run No. 11RS, it should be noted that there was no net removal of nitrate during the roughing regeneration. This is not easy to understand in light of the proportionately higher concentration of chloride in this spent regenerant. Sulfate and nitrate eluted during the polishing regenerations are shown in Figures 11R2, 13R2, 14R2 and 15R2. From the polishing regeneration figures, it can be seen that the second regeneration with fresh regenerant takes as long to reduce the NO_3-N concentration to 200 mg/L as a single step regeneration would.

Thus, if the objective is to achieve a complete regeneration, a roughing regeneration using spent, nitrate-contaminated regenerant followed by a polishing step with pure NaCl offers no advantage over a single-step regeneration with pure NaCl. Nevertheless, since a net 50% removal of nitrate occurs during the roughing regeneration, the procedure might offer an advantage when the objective is partial, rather than complete, regeneration of the exhausted bed. Unfortunately we did not study partial regeneration with spent regenerants so the hypothesis remains unproven but worthy of future study.

Partial Regeneration

The Partial Regeneration Method--

Guter's study [7] of nitrate removal from well water in McFarland, California showed that the amount of salt required for regeneration is substantially reduced when the resin bed is only partially regenerated between exhaustion runs. In complete regeneration, NaCl solution is pumped through the exhausted bed until all the nitrate has been eluted. During this process, the divalent sulfate ion, which is least preferred at the high ionic strength of the regenerant solution, is removed first. Displacing the nitrate remaining on the column becomes increasingly difficult as the fraction of the bed in the nitrate form decreases. More equivalents of salt per equivalent of nitrate are required as regeneration nears completion.

The technique of partial regeneration involves leaving some nitrate on the resin bed. After partial regeneration a backwash is used to mix the resin beads so that the nitrate, originally concentrated in a zone at the outlet end of the column, is uniformly distributed throughout the bed. During the next exhaustion run, there should be a steady leakage of nitrate prior to breakthrough. Guter [7] presents formulas for calculating the required regeneration level for a given feed water composition and a desired effluent nitrate concentration.

Choosing an acceptable nitrate leakage of 7.5 mg/L (75% of the 10 mg/L MCL) and using Guter's methodology, one can calculate that a regeneration level of 0.71 equivalents salt per equivalent resin should be able to reduce the NO_3-N concentration of 314 bed volumes of Glendale water from 19.2 to 7.5 mg/L. We did not, however, find this to be the case; more salt than this was needed.

Partial Regeneration Results in Field and Lab Tests--

Glendale-pilot plant tests confirmed the economic advantage of partial regeneration, but the actual regeneration level required and the initial nitrate leakage observed with the Glendale water were considerably higher than predicted from Guter's methodology. Regeneration levels from 0.64 to 2.0 equiv. Cl^-/equiv. resin were tested. Figure 10 compares the Glendale nitrate breakthrough curves following complete and partial regenerations with 1.0 N salt. It is apparent that 0.64 equivalents of salt per equivalent of resin is insufficient to produce a reasonable run length, but that a regeneration level of 1.0 or higher is acceptable if one disregards (because it can be eliminated) the excessive nitrate leakage during the initial 75 BV of effluent.

We tried extensive backwashing of the partially regenerated bed as suggested by Guter [6] to eliminate the initial high-nitrate leakage. This was not successful, however, as is evident in Figure 10. The successful elimination of excessive leakage can be seen in Figure 11 where the performance of a partially regenerated but unmixed bed is compared to that of a well-mixed homogeneous bed. The elimination-of-leakage experiments depicted in Figure 11 were performed in small laboratory columns using simulated Glendale water. Following exhaustion and partial regeneration with 1.0 equiv. Cl^-/equiv. resin, the unmixed bed was simply exhausted again while the resin in the other column was removed, manually mixed and placed back into the column prior to the exhaustion run shown. It is evident that thorough mixing will eliminate the excess nitrate leakage at the beginning of an exhaustion following a cocurrent (downflow) partial regeneration. But backwashing will not achieve this mixing because the resin bed remains classified with the largest resin beads on top and the smallest on the bottom.

There was a question to be answered regarding the expected shape of the nitrate breakthrough curve from a partially regenerated, homogeneous bed. This question was answered using a mathematical model [18] based on Helfferich's Multicomponent Chromatography Theory [4]. Such predictions are not trivial because a partially regenerated resin is presaturated, not with chloride only, but with a mixture of chloride and nitrate (typically 80% Cl^- and 20% NO_3^-). The predicted nitrate leakage from

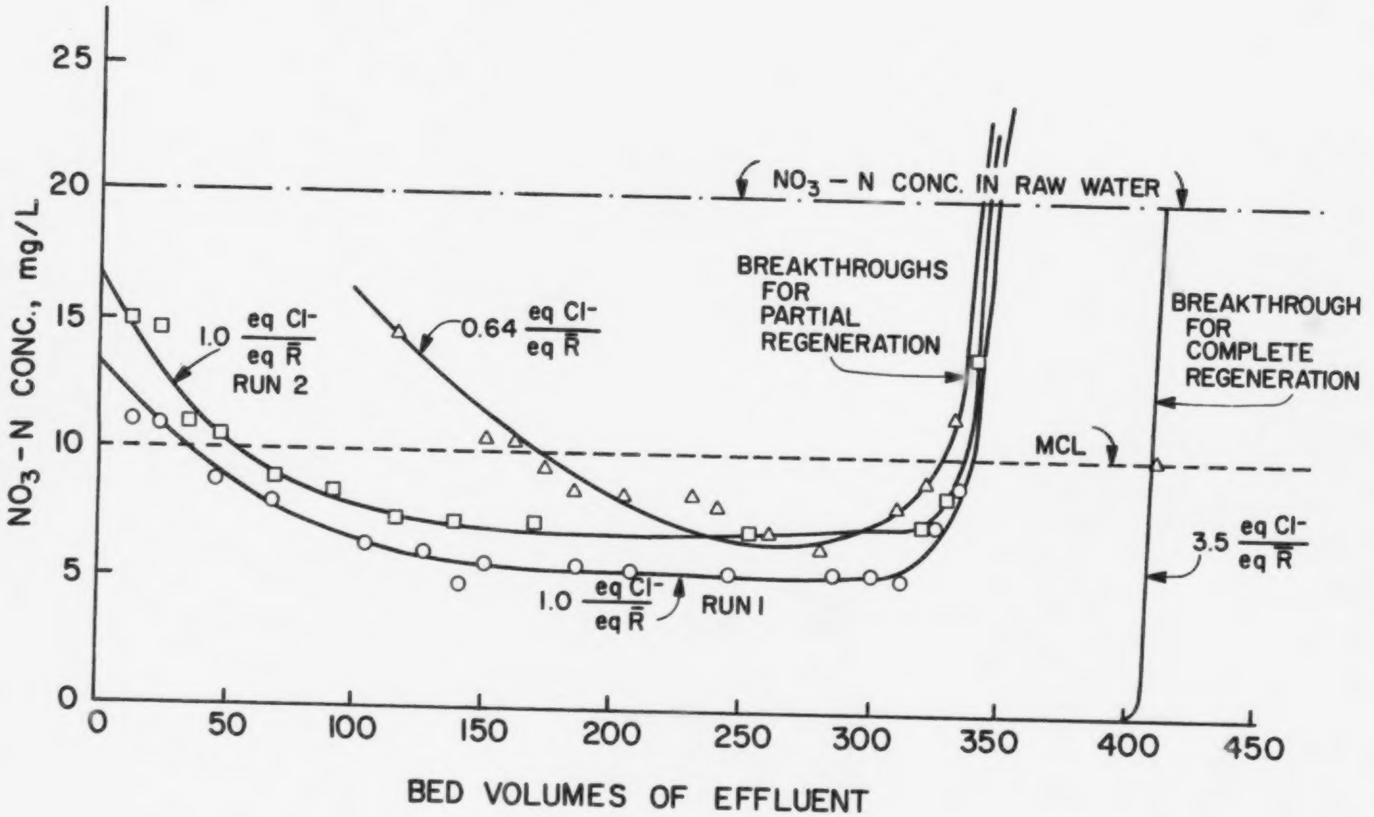


Figure 10. Nitrate breakthrough curves for completely and partially regenerated beds.

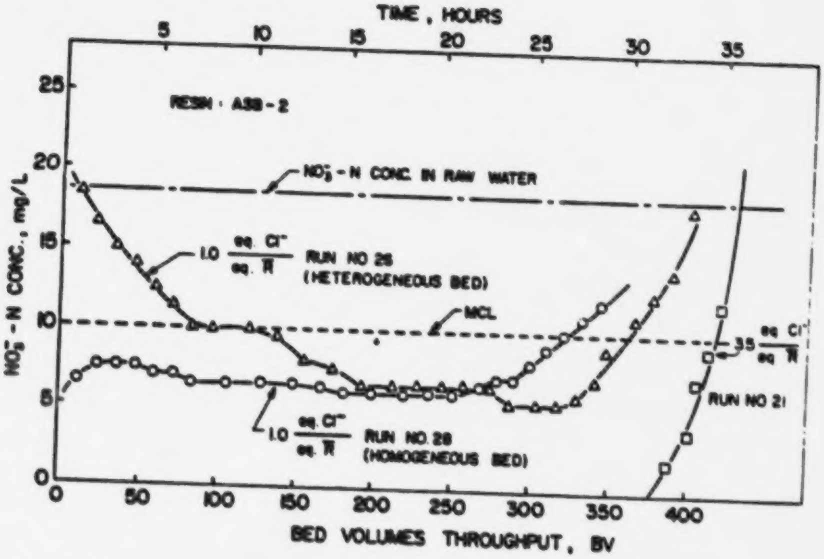


FIGURE 11. Nitrate breakthrough curves following complete regeneration (3.5 eqiv. Cl^-/equiv. resin) and partial regeneration (1.0 equiv. Cl^-/equiv. resin) with and without resin mixing. Column feed is simulated Glendale water.

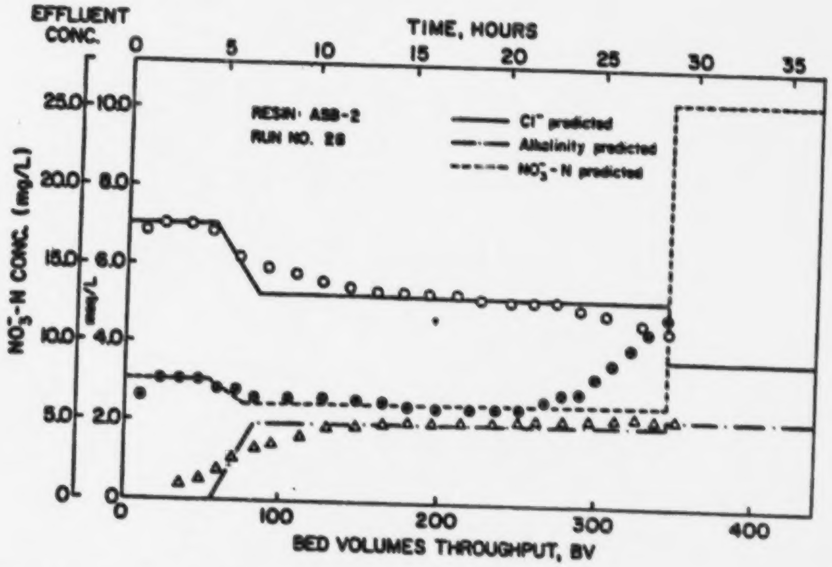


FIGURE 12. A comparison of predicted and actual concentration histories for ions emanating from a partially regenerated bed receiving simulated Glendale water feed.

such columns is not constant as can be seen in Figure 12--a comparison of the actual and predicted effluent histories from a partially regenerated bed receiving simulated Glendale feed water. It is evident that the model which requires only the initial resin composition, the feedwater composition, the resin capacity and separation factors for nitrate, sulfate, chloride and bicarbonate, does a good job of predicting the nitrate, chloride and bicarbonate effluent histories. The potential use of such a model for partial regeneration calculations is apparent.

Table 17 shows the regenerant requirement (equivalents of NaCl regenerant per equivalent of nitrate removed from the feed water on subsequent exhaustion) as a function of regenerant level. It can be seen that for the Glendale water, 1.0 equivalent salt per equivalent resin is the optimum for partial regeneration with 1.0 N salt. Below this level, run length is too short due to high initial nitrate leakage. Above this level, too much nitrate is removed from the resin and the increasing difficulty of nitrate removal leads to diminishing efficiency.

TABLE 17
EFFECT OF REGENERATION LEVEL (EQ SALT/EQ RESIN) ON PARTIAL REGENERATION WITH 1.0N SALT

Regeneration Run No.	Regeneration Level (eq salt/eq resin)	Eq. Cl^- regenerant Eq. NO_3^- Removed From Feed
18RP	0.64	6.8
17RP	1.0	5.9
27RP	2.0	6.8

After 1.0 equivalent salt per equivalent resin had been established as an acceptable level of regeneration, two different regenerant concentrations (.25 and .50 N NaCl) were used to achieve this level. Table 18 indicates that, at least within experimental error, there is no significant difference in the efficiency of partial regeneration with salt concentration varied from .25 to 1.0 N. This result is surprising in light of the experimental findings for complete regeneration, for which the most dilute regenerant gave the most efficient regeneration.

Upflow (Counterflow) Partial Regeneration--

Direction of regenerant flow is another variable that may affect regeneration efficiency. Downflow regeneration was used for most of the Glendale work, but upflow was tested for comparison because there is a general rule in demineralization and softening that counterflow regeneration is more efficient. It was observed that the nitrate concentration of the product water after partial regeneration with 0.5 N salt to a regeneration level of 1.0 exceeded the MCL of 10 mg/L throughout the run. Upflow partial regeneration is clearly less efficient than downflow. This is due to the chromatographic nature of the column. At exhaustion, nitrate is concentrated in a zone at the exit end of the column and sulfate occupies a zone at the inlet end. When regenerant is pumped in the same direction as the original feed flow, the sulfate is pushed down the column and helps to displace nitrate. With upflow regeneration, this advantage is lost and the nitrate must travel through the entire length of the bed to reach the new outlet. Furthermore, our pilot columns were not designed to hold the resin firmly in place during upflow regeneration. Due to the very similar densities of the anion resin and the salt solution, slight expansion of the bed and poor regenerant flow distribution may have resulted in a less than optimum regeneration.

TABLE 18
EFFECT OF NaCl CONCENTRATION ON PARTIAL REGENERATION TO 1.0 EQ SALT/EQ RESIN

Regeneration Run No.	NaCl Concentration (N)	$\frac{\text{Eq. Cl}^- \text{ regenerant}}{\text{Eq. NO}_3^- \text{ Removed From Feed}}$
25RP	0.25	5.9
26RP	0.25	6.1
19RP	0.5	5.6
20RP	0.5	5.6
16RP	1.0	4.6
17RP	1.0	5.9

COMPARISON OF COMPLETE AND PARTIAL REGENERATION

After it was discovered that the early, excess nitrate leakage could be eliminated by efficiently mixing the resin following a partial regeneration, the method looked quite attractive. The experimental data for 1.0 equiv. Cl^-/equiv. resin showed the partial regeneration to be more efficient than complete regeneration even with the dilute 0.25 N regenerant. For this reason, a detailed comparison between the methods was made; the results are presented in Table 19.

Although 1.0 equiv. Cl^-/equiv. resin was the partial regeneration level used in most of the pilot runs, a careful examination of the nitrate effluent histories led to the conclusion that slightly more chloride would be needed to achieve the maximum desirable leakage of 7.0 ppm NO_3-N. It was estimated that a level of 1.2 equiv. Cl^- per equiv. of spent resin would consistently produce 330 BV of acceptable effluent. Thus, these values were used in the comparison.

In Table 19 it may be seen that the advantages of partial regeneration are (a) it is more efficient in terms of equiv. of Cl^- required per equiv. of nitrate removed (4.84 compared to 6.65), (b) it produces much less wastewater (1.1% compared to 3.0%), and (c) for a 1.0 mgd plant it uses 890 lbs/day (404 kg/day), i.e. 37%, less salt for regeneration. Finally, partial regeneration eliminates the need for bypass blending and its attendant complexities.

The use of complete regeneration with a dilute 0.25 N regenerant produces 2.5 times as much wastewater but it is approximately one half as concentrated. Complete regeneration allows pH detection of nitrate breakthrough, whereas significant, useful pH changes accompanying nitrate breakthrough were not observed following partial regeneration (more study is required, however). An additional disadvantage of partial regeneration is the need for thoroughly mixing the resin following regeneration so as to avoid excessive nitrate leakage.

COMPARATIVE COSTS OF NITRATE REMOVAL

Rough cost estimates for nitrate removal were made [6] assuming that the pilot scale finding could be put into commercial practice. The 1983 updated costs, listed in Table 20, are based on comparisons to previous work [3,7] for ion exchange and on references [19,20] for membrane processes. As expected, membrane processes are much more expensive and they produce an unnecessarily low TDS product water. However for nitrate removal from waters containing more than 1000 ppm TDS, the membrane processes may be the only reasonable alternatives. In this case, electrodialysis would tend to be preferred over reverse osmosis. The rough cost estimates include amortized capital, labor, chemicals, resin and membrane replacement, and energy. The example feedwater contains 21 ppm NO_3-N, which is 2.1 times the EPA MCL but still less than 22.6 ppm NO_3-N, which is the WHO recommended limit [21]. Wastewater disposal costs are not included in the estimates.

TABLE 19
COMPARISON OF OPTIMUM COMPLETE AND PARTIAL REGENERATIONS FOR GLENDALE WATER

Description	Complete Regeneration	Partial Regeneration
Regenerant conc., N	0.25	1.0
Equiv. Cl^-/Equiv. Resin	3.0	1.2
Equiv. Cl^-/Equiv. NO_3-N removed	6.65	4.84
Run length to NO_3^- breakthrough, BV	400.0	330.0
Run length at 20 BV/hr, hrs	20.0	16.5
Regenerant volume, BV	16.0	1.6
Slow rinse volume, BV	2.0	2.0
Wastewater volume, BV	18.0	3.6
Wastewater volume as a % of blended product water	3.0	1.1
Wastewater sodium conc., mg/L	5,110.	10,200.
Wastewater chloride conc., mg/L	6,000.	10,100.
Wastewater nitrate conc., mg/L	2,010.	5,170.
Wastewater sulfate conc., mg/L	960.	3,600.
Wastewater TDS conc., mg/L	14,100.	29,070.
Bypass flow, percentage of feed	33.0	none
pH detection of NO_3^- breakthrough?	yes	no
Requires resin mixing following regeneration?	no	yes
NaCl consumption for 1.0 mgd blended product water, lb/day	3,250.	2,360.
kg/day	1,480.	1,070.
Wastewater volume for 1.0 mgd blended product water, gal/day	30,000.	11,000.
m^3 day	114.	41.7

Notes: Ions in raw water used to make up regenerant solutions are not included in chemical analysis. Nitrate concentration is given as NO_3^-, not NO_3-N. Feedwater is Glendale water with 21 ppm NO_3-N. Product water from both processes contains 7.0 ppm NO_3-N as an average. In practice, complete regeneration with higher, e.q. 0.5-1.0 N NaCl, concentration followed by an appropriate amount of slow rinse might produce a chloride efficiency equal to 0.25 N with less wastewater volume produced.

TABLE 20
APPROXIMATE COSTS FOR NITRATE REMOVAL BY IX, ED AND RO

Process	$/1000 gal.	$\$/m^3$	Product Water TDS, ppm
Single-Bed Chloride-Form Ion Exchange	0.3	0.08	500
Electrodialysis	0.85	0.22	185
Reverse Osmosis (Aramid Membrane)	1.00	0.26	185

Assumptions: Feedwater = 500 ppm TDS
21 ppm NO_3-N
50 ppm $SO_4^{=}$
Bypass flow = 30% of blended product flow
Desalting process = 90% overall TDS rejection
NO_3-N = 7 ppm in blended product

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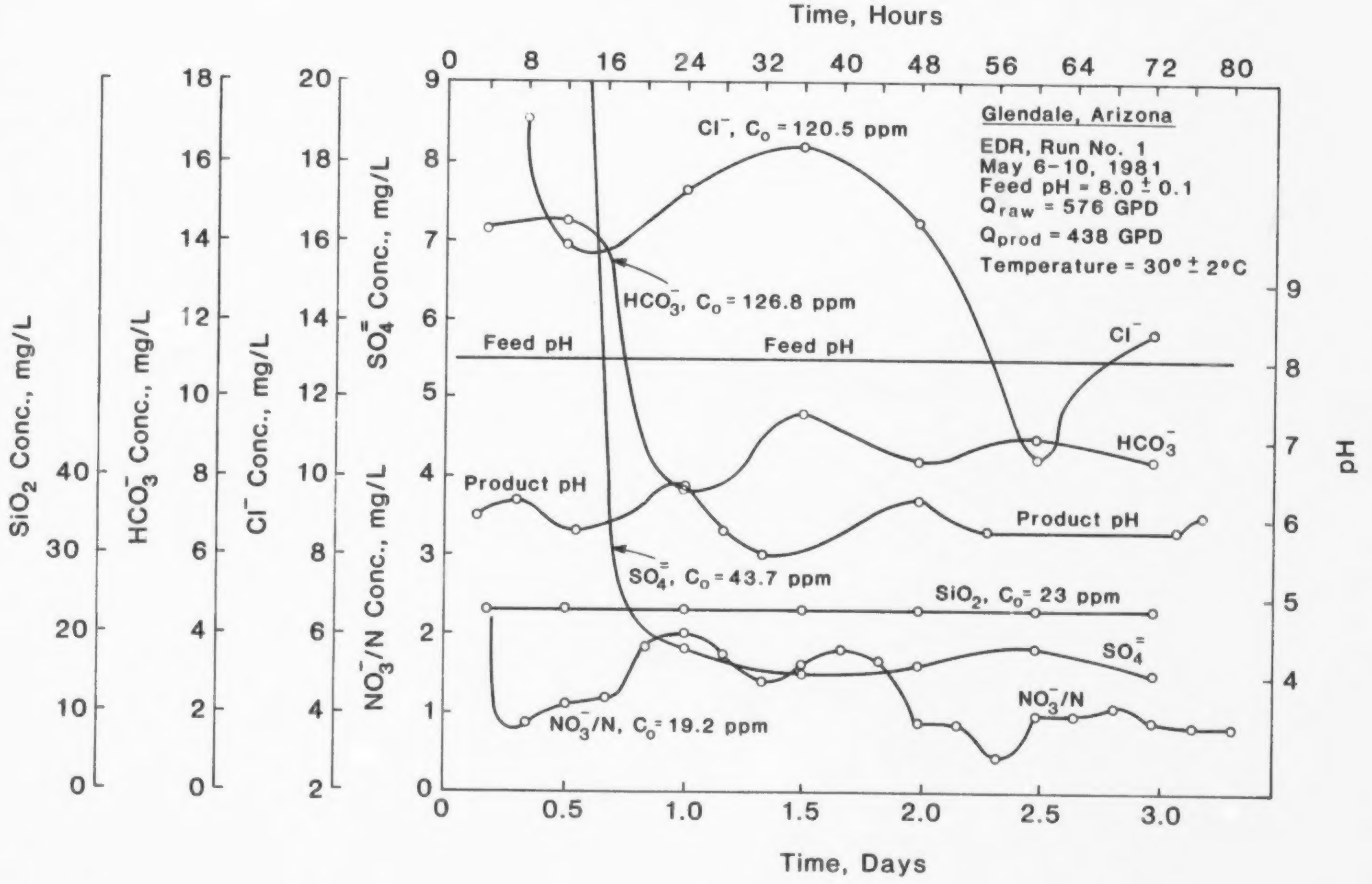


Figure A-1. Product water quality from the 80-hour electrodialysis run with Ionics Aquamite I EDR unit.

APPENDIX B

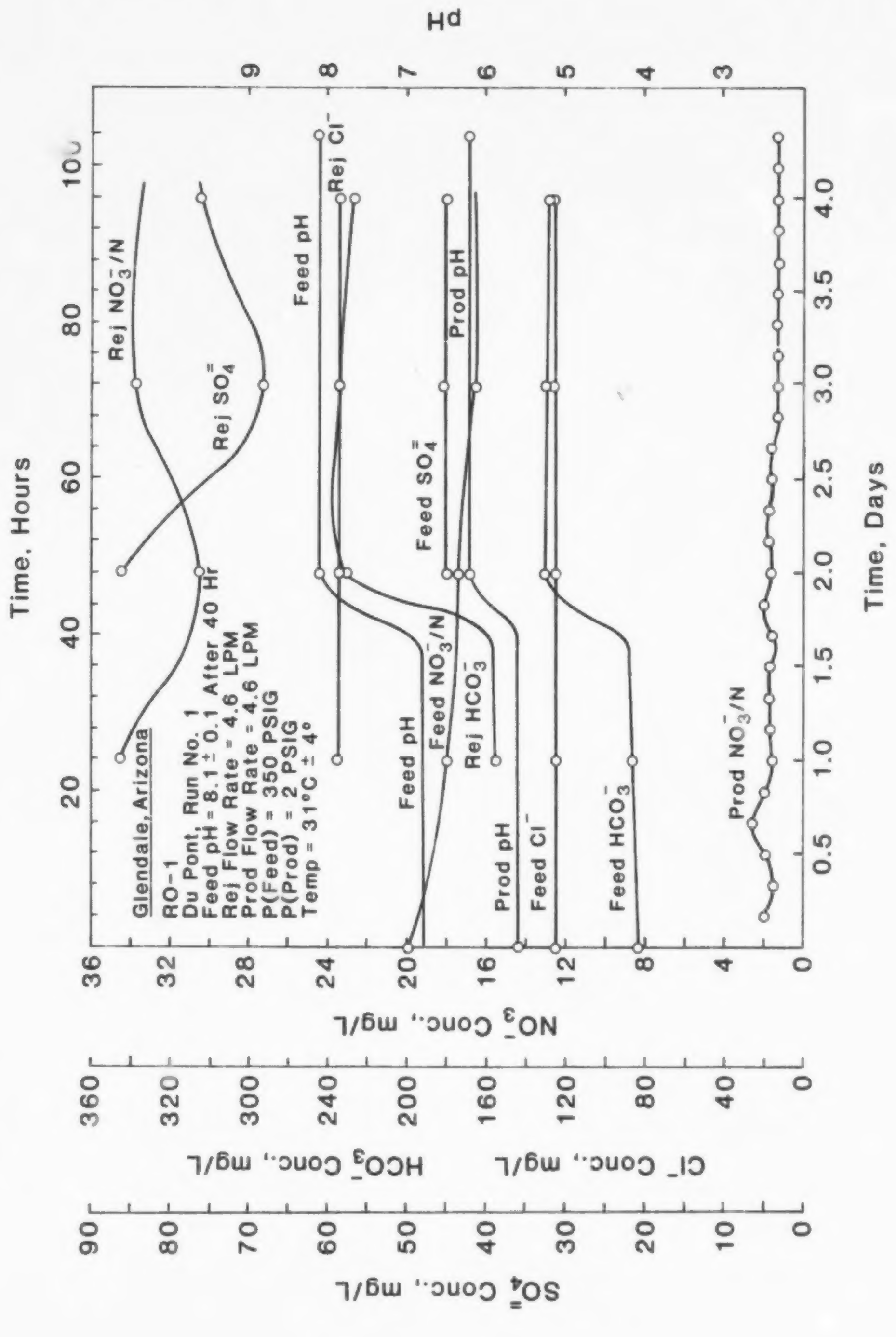


Figure B-1. Feed, product and reject water quality from the 125-hour DuPont RO run.

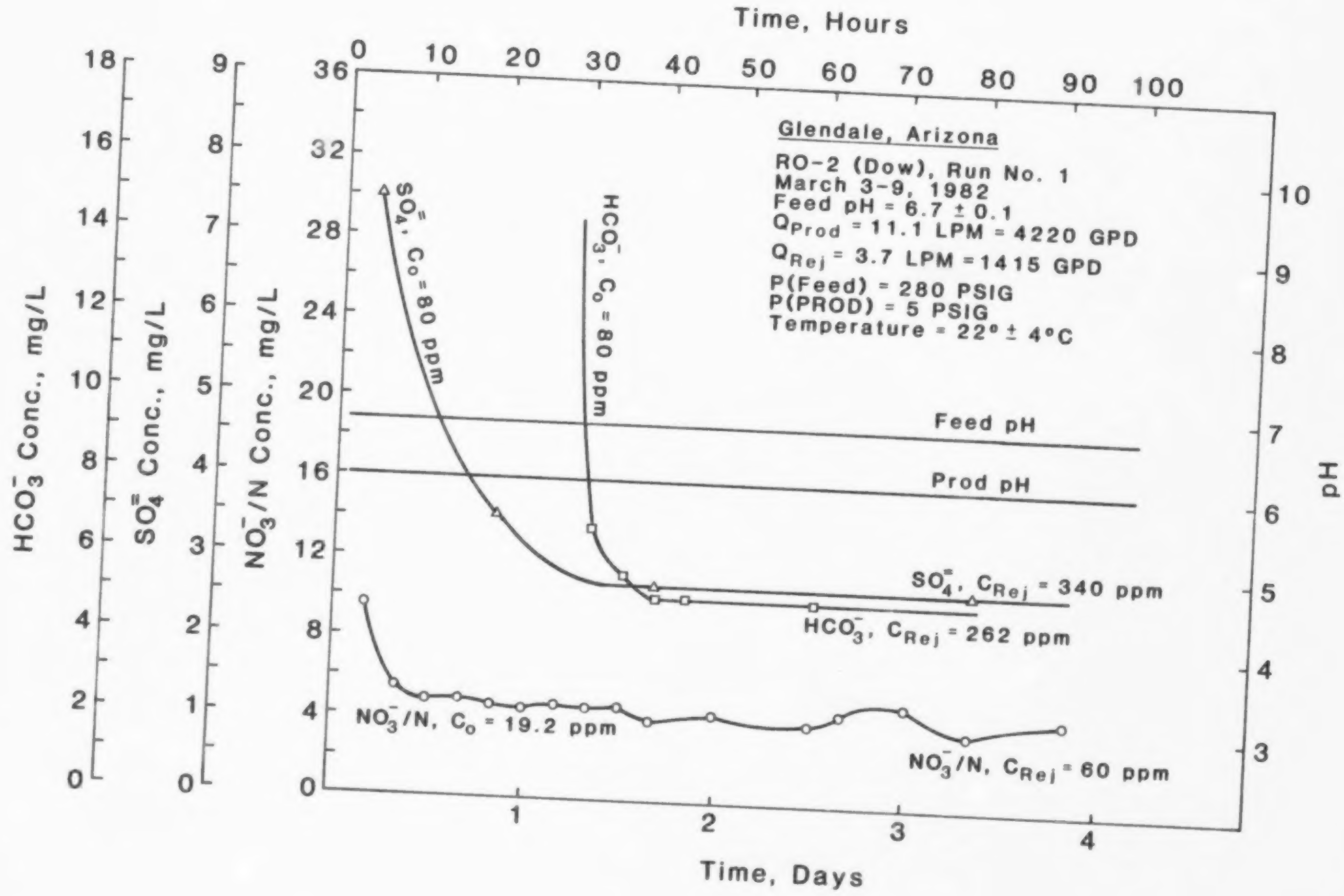


Figure B-2. Feed, product and reject water quality from the 125-hour Dow RO run.

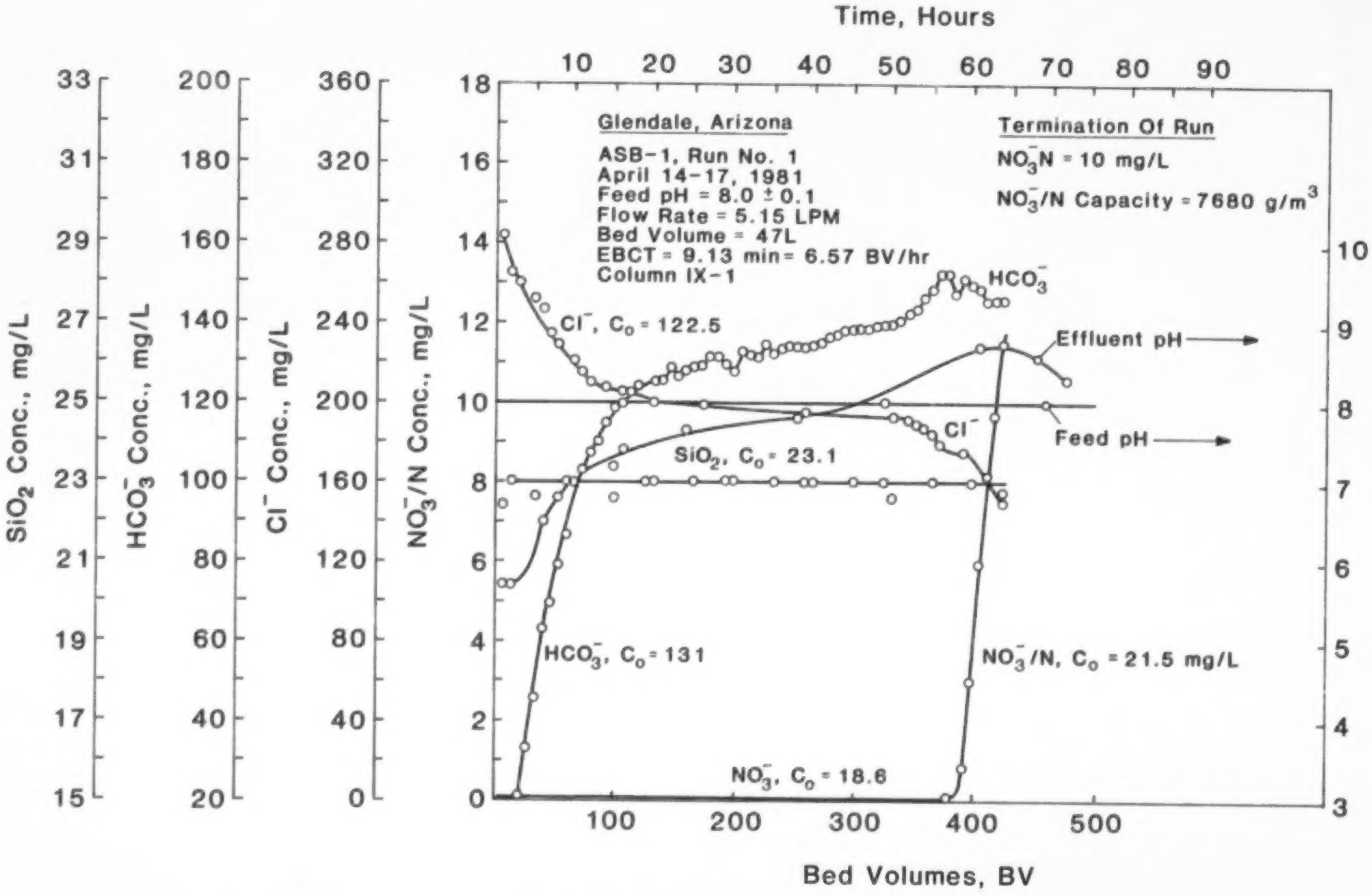


Figure C-1. Exhaustion Run No. 1 using quaternary type 1 resin (ASB-1) 9.13 min. EBCT

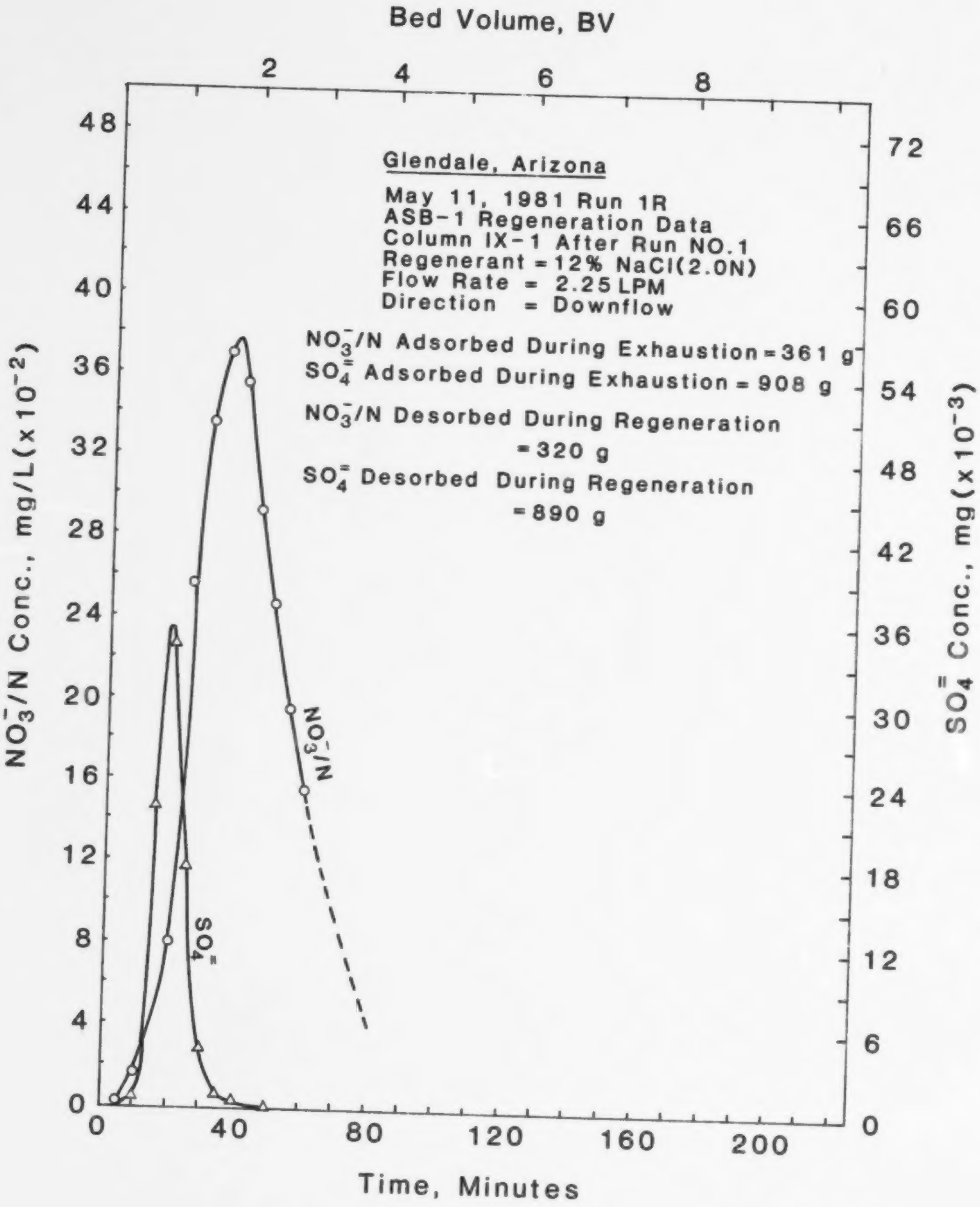


Figure C-1R. Complete regeneration Run No. 1R with 2.0N NaCl following exhaustion Run No. 1.

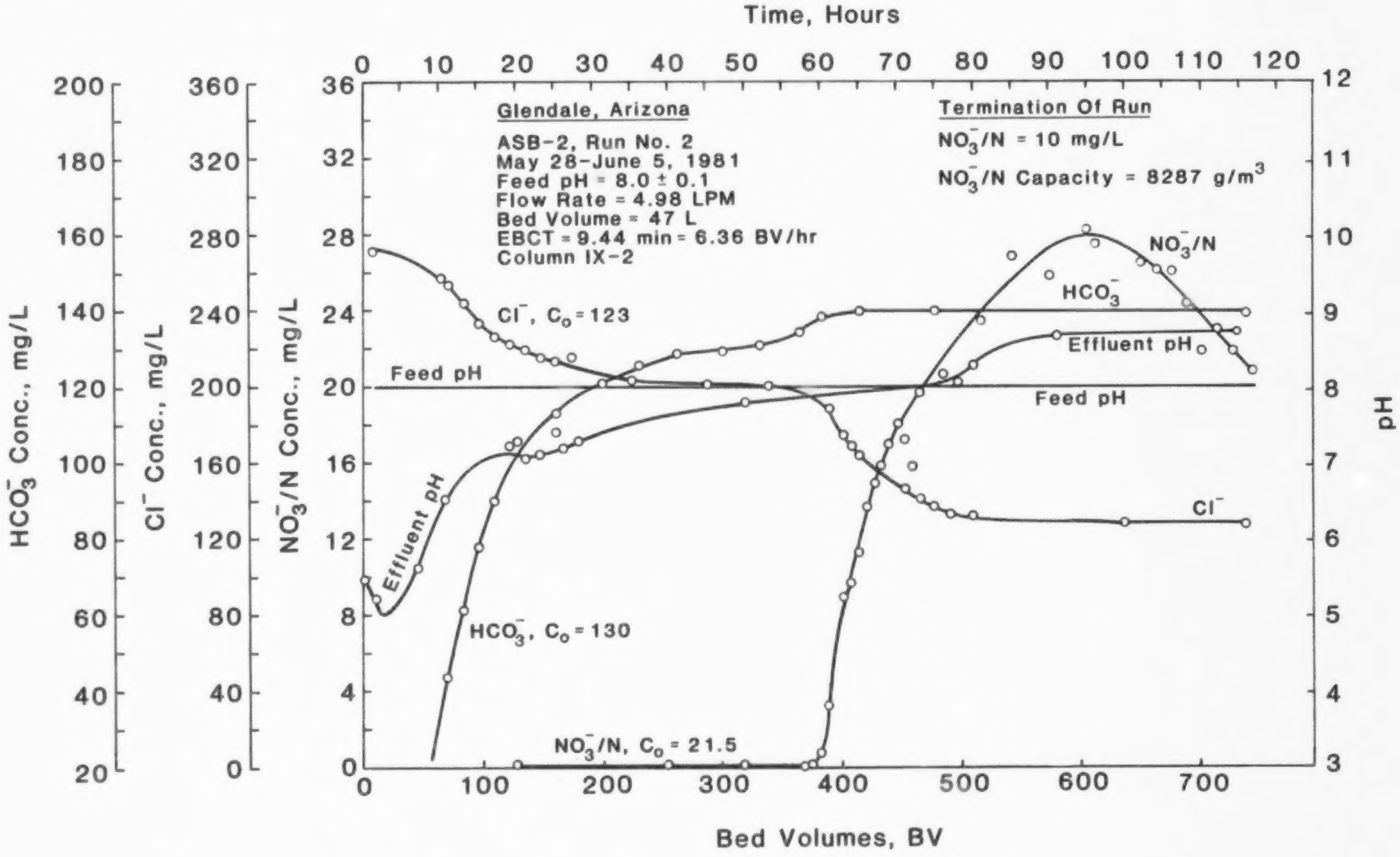


Figure C-2. Exhaustion Run No. 2 using quaternary type 2 resin (ASB-2) 9.44 min. EBCT.

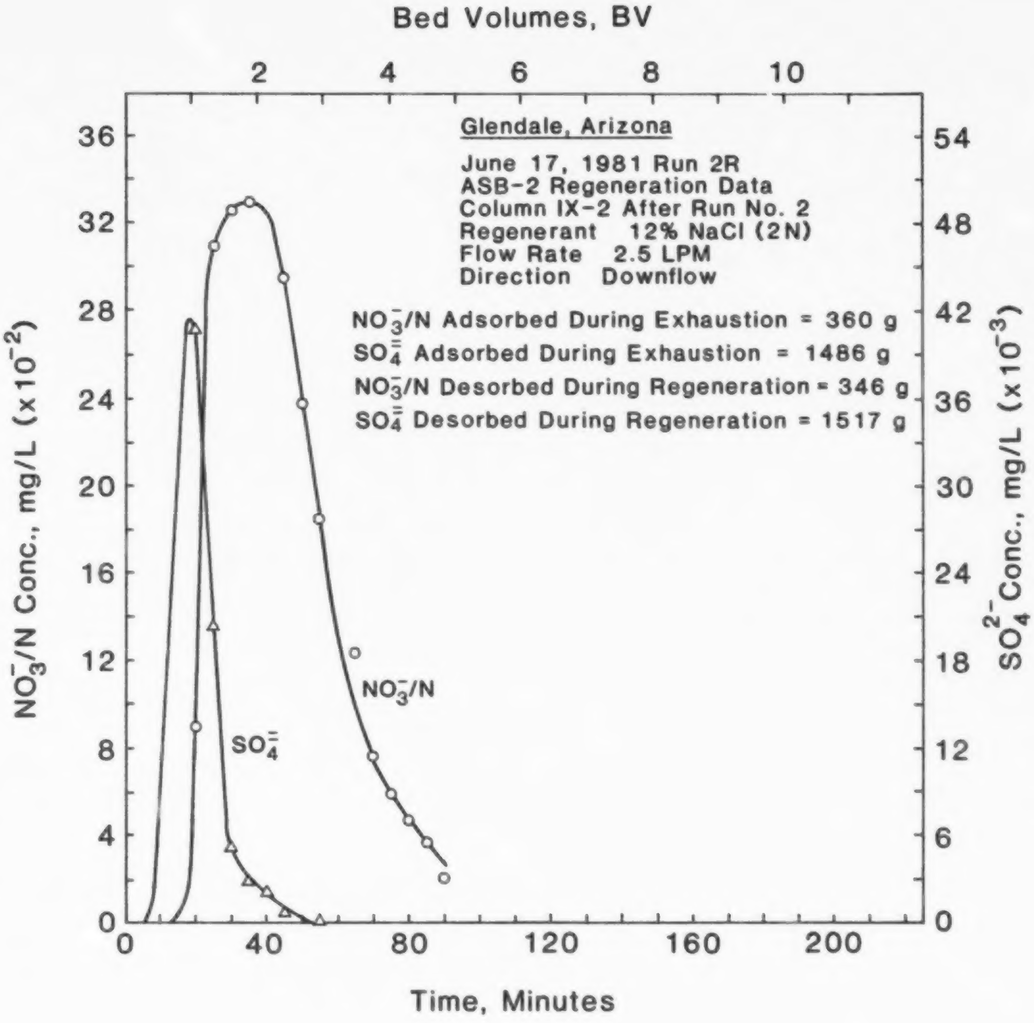


Figure C-2R. Complete regeneration Run No. 2R using 2.0N NaCl following Run No. 2.

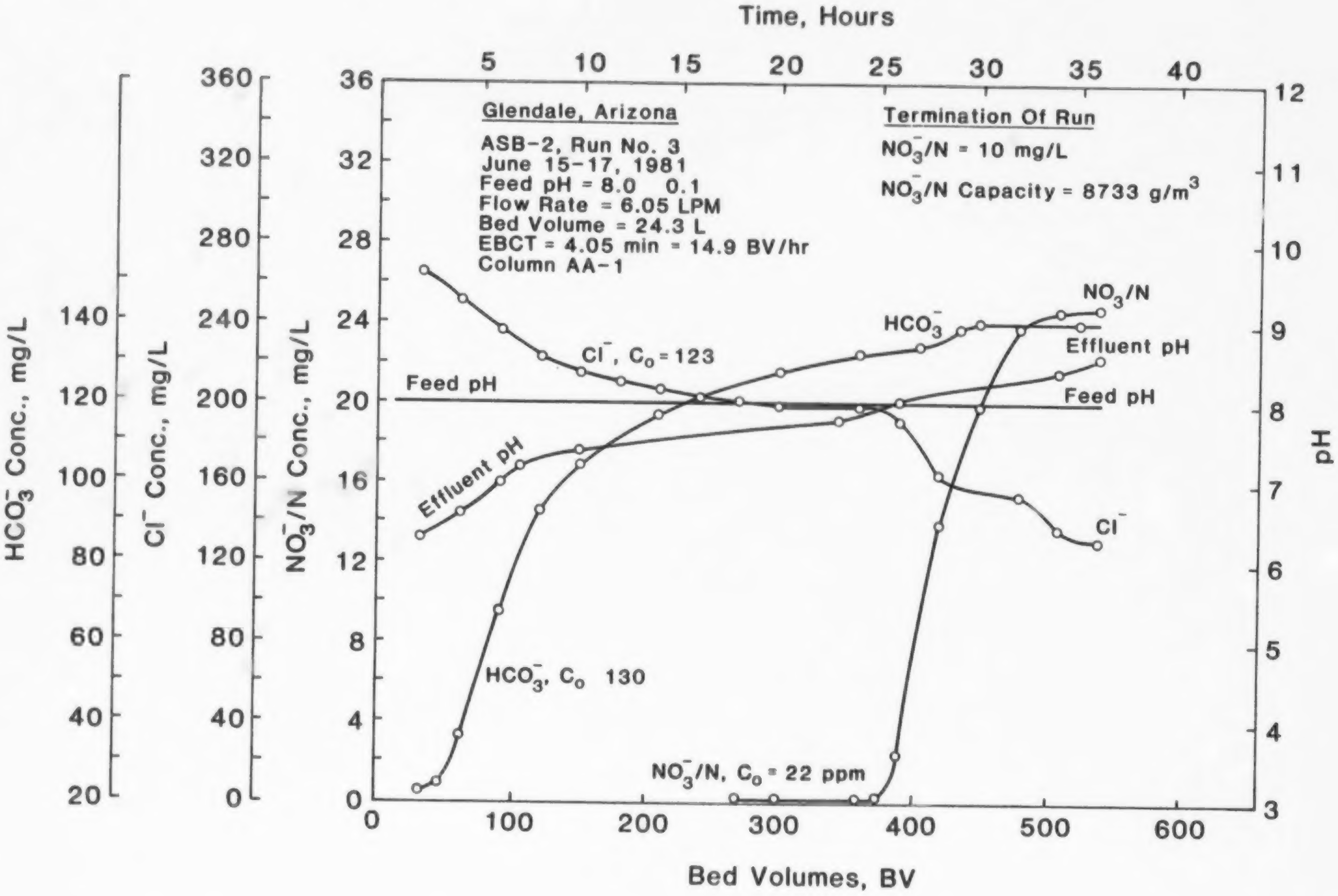


Figure C-3. Exhaustion Run No. 3 using quaternary type 2 resin (ASB-2) 4.05 min. EBCT.

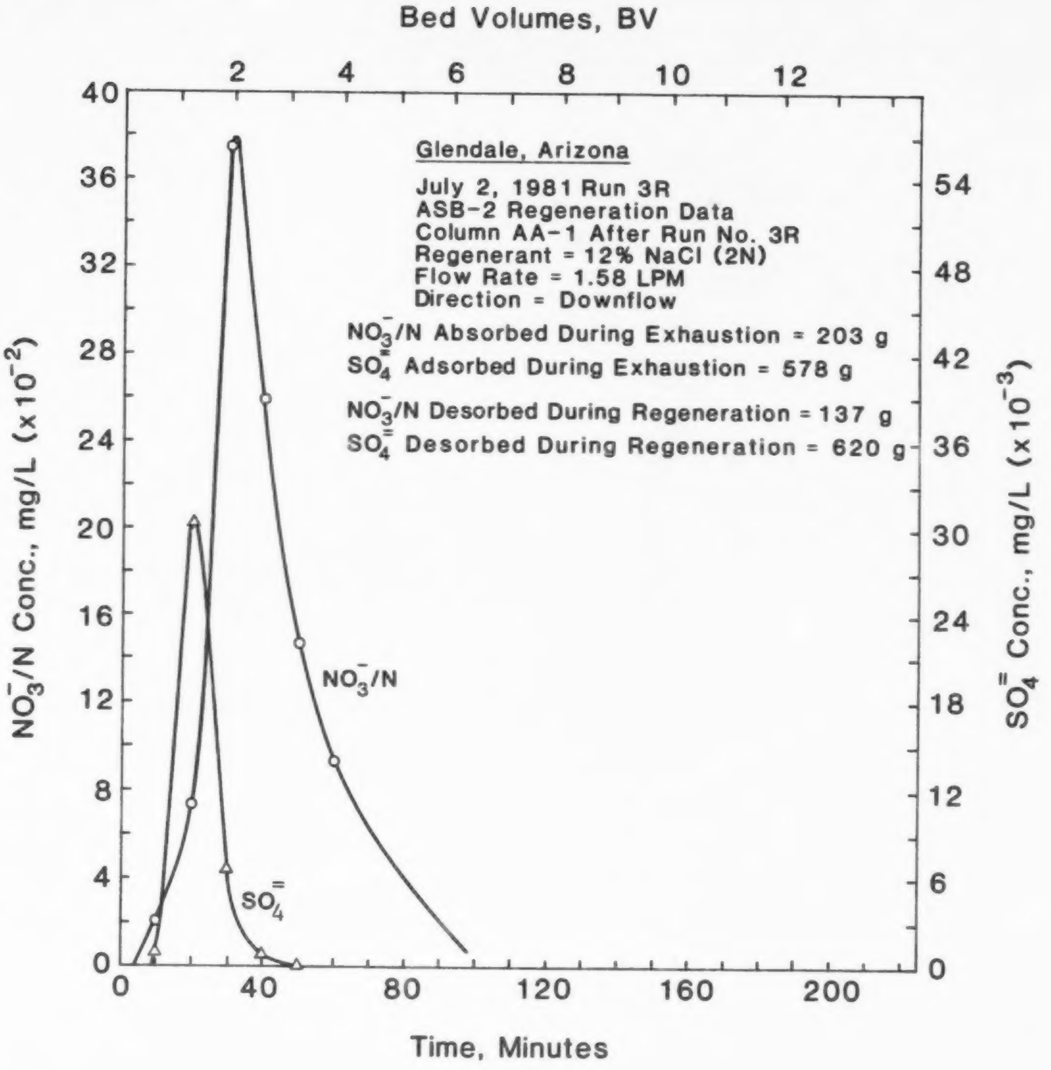


Figure C-3R. Complete regeneration Run No. 3R using 2.0 N NaCl.

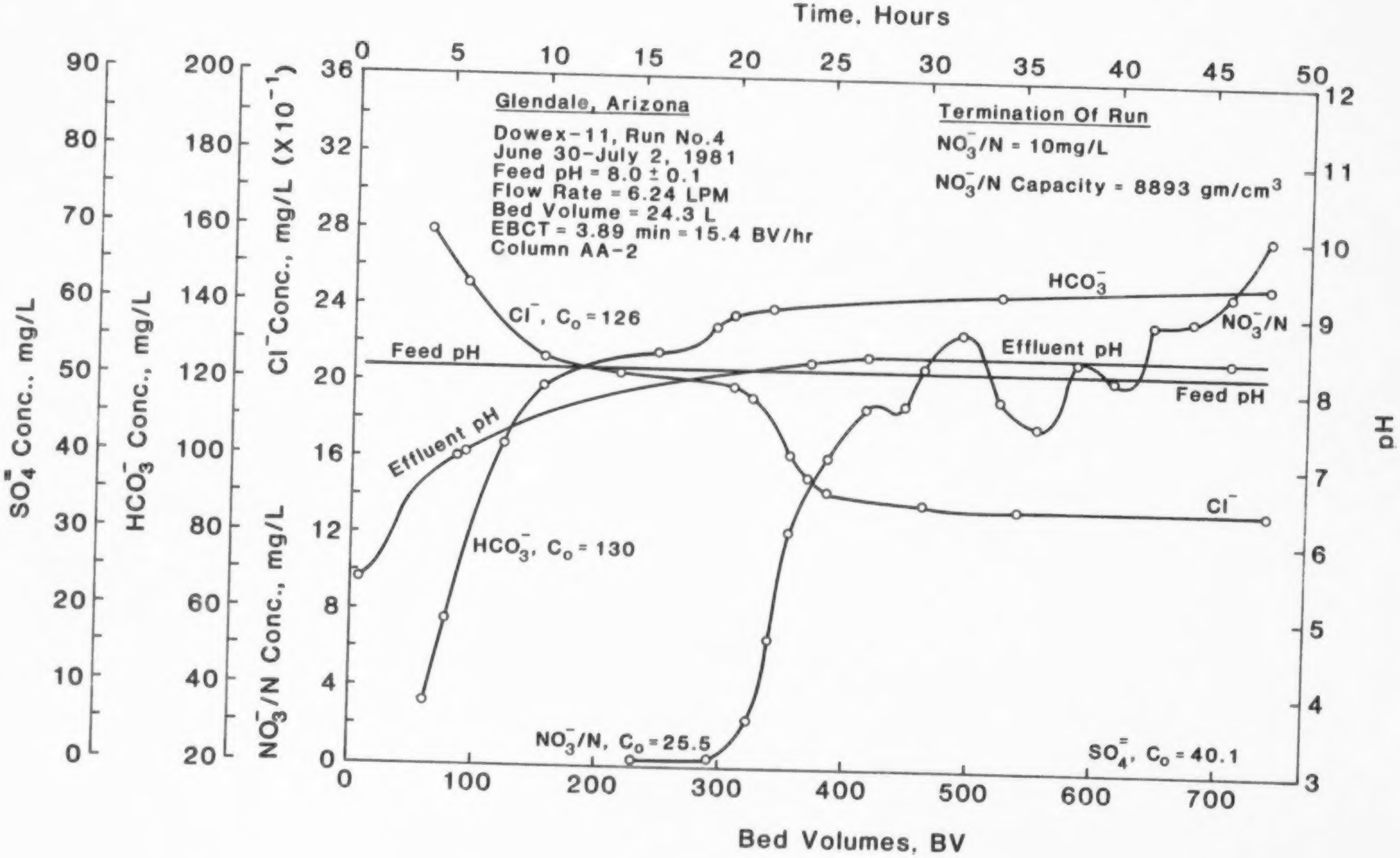


Figure C-4. Exhaustion Run No. 4 using quaternary type 1 isoporous resin (Dowex 11), EBCT 3.89 min.

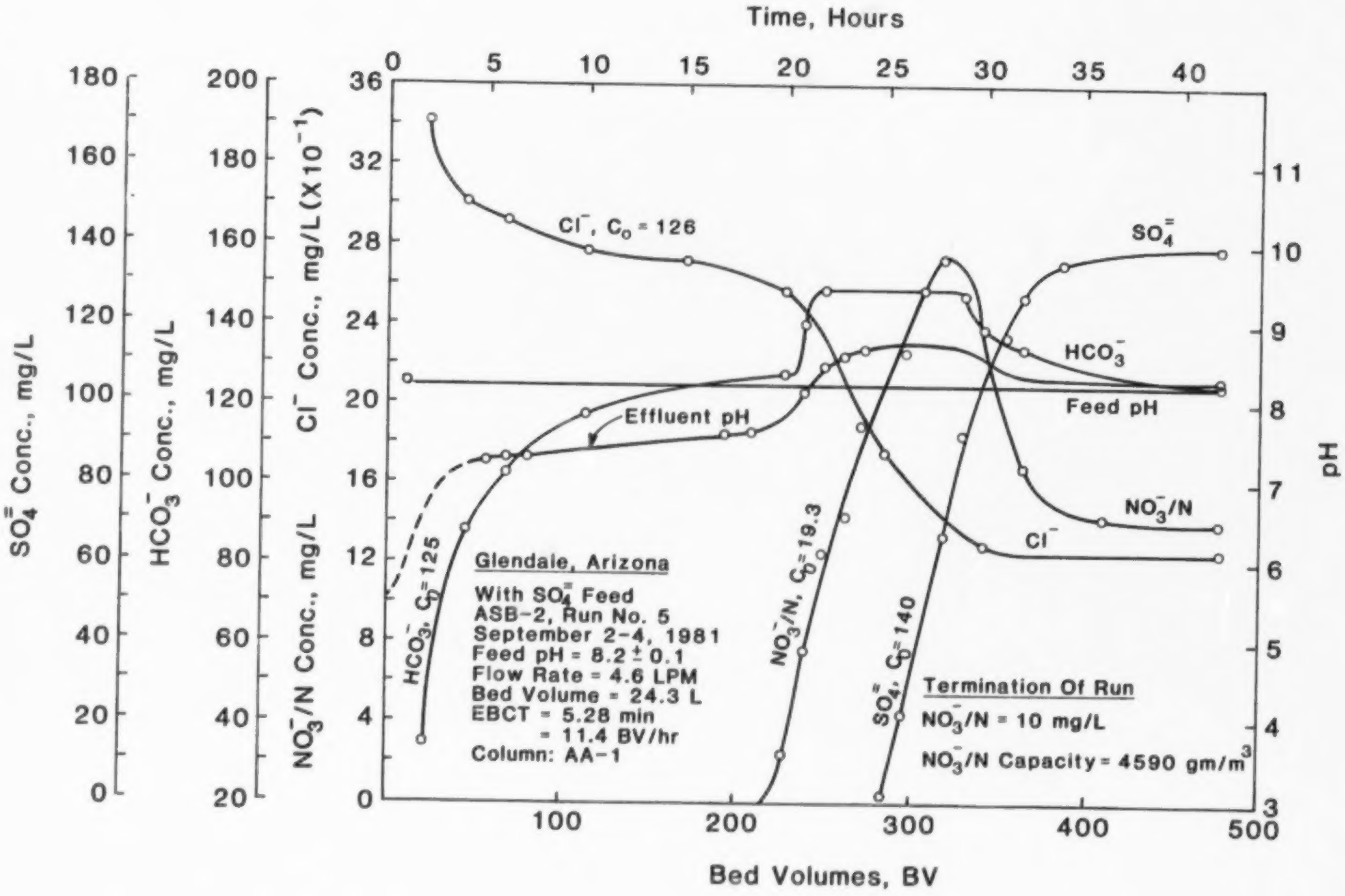


Figure C-5. Exhaustion Run No. 5 using quaternary type 2 resin (ASB-2) EBCT 5.28 min.

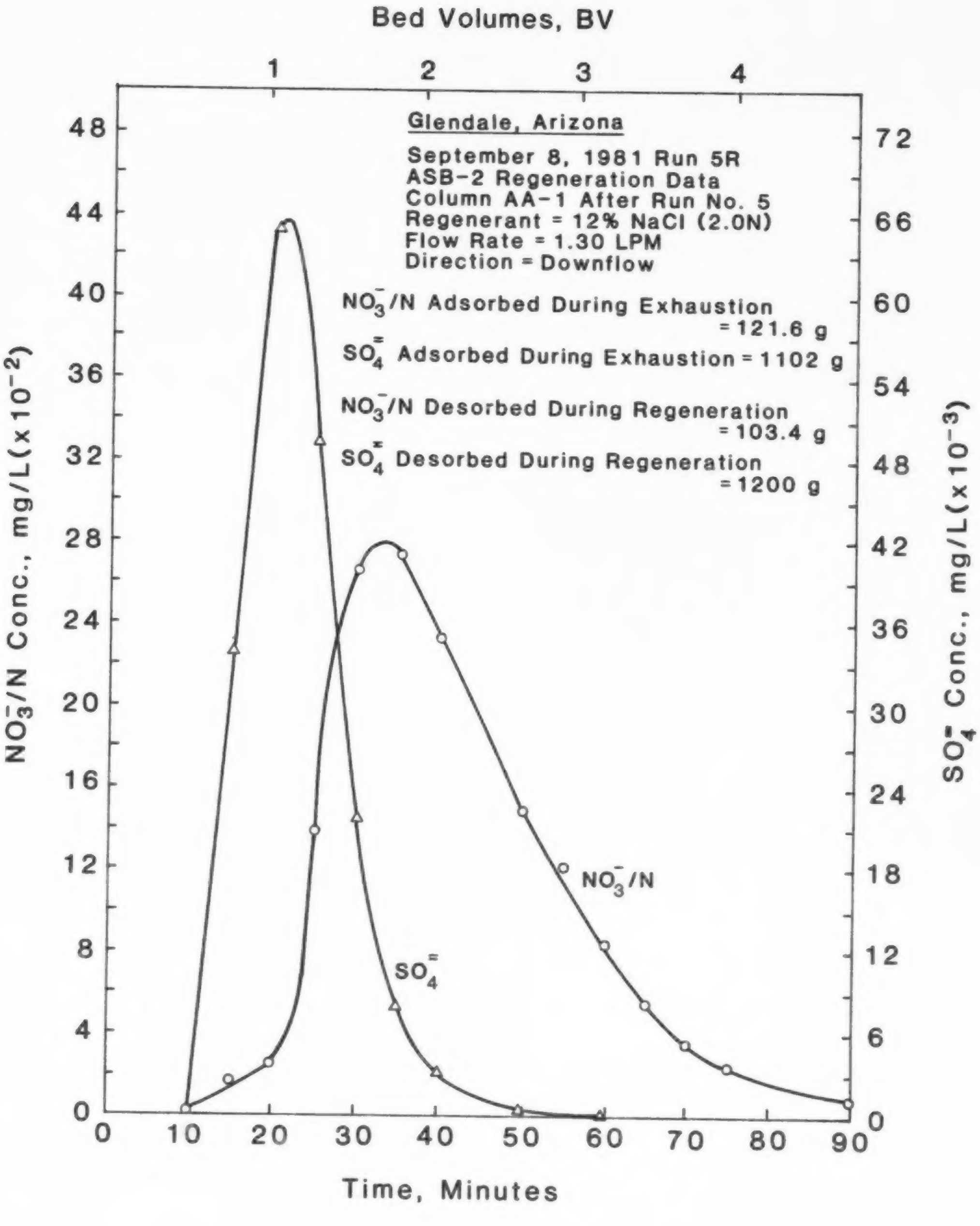


Figure C-5R. Complete regeneration Run No. 5R using 2.0 N NaCl.

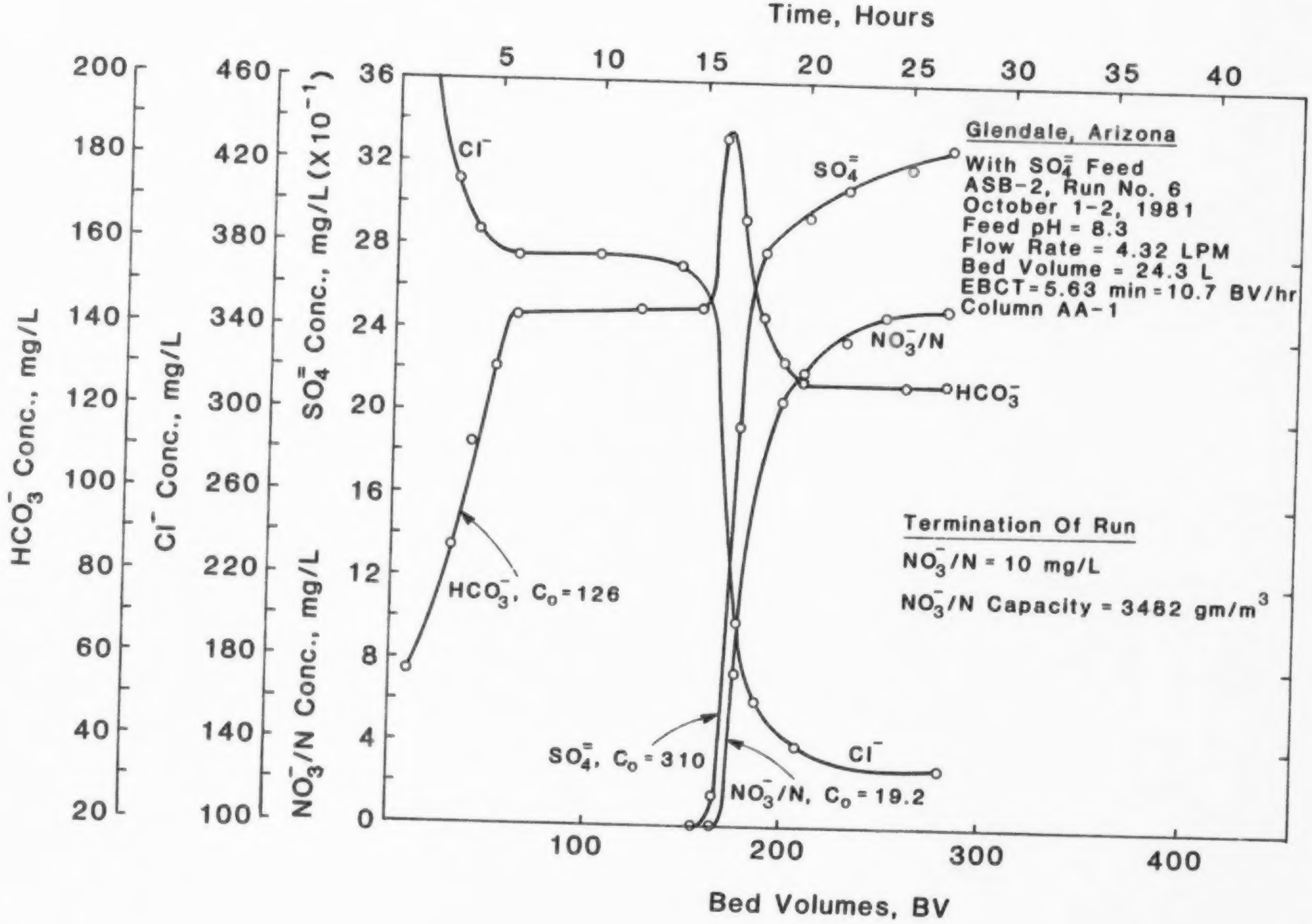


Figure C-6. Exhaustion Run No. 6 using ASB-2 resin with high sulfate feed (310 mg/L), EBCT = 5.63 min.

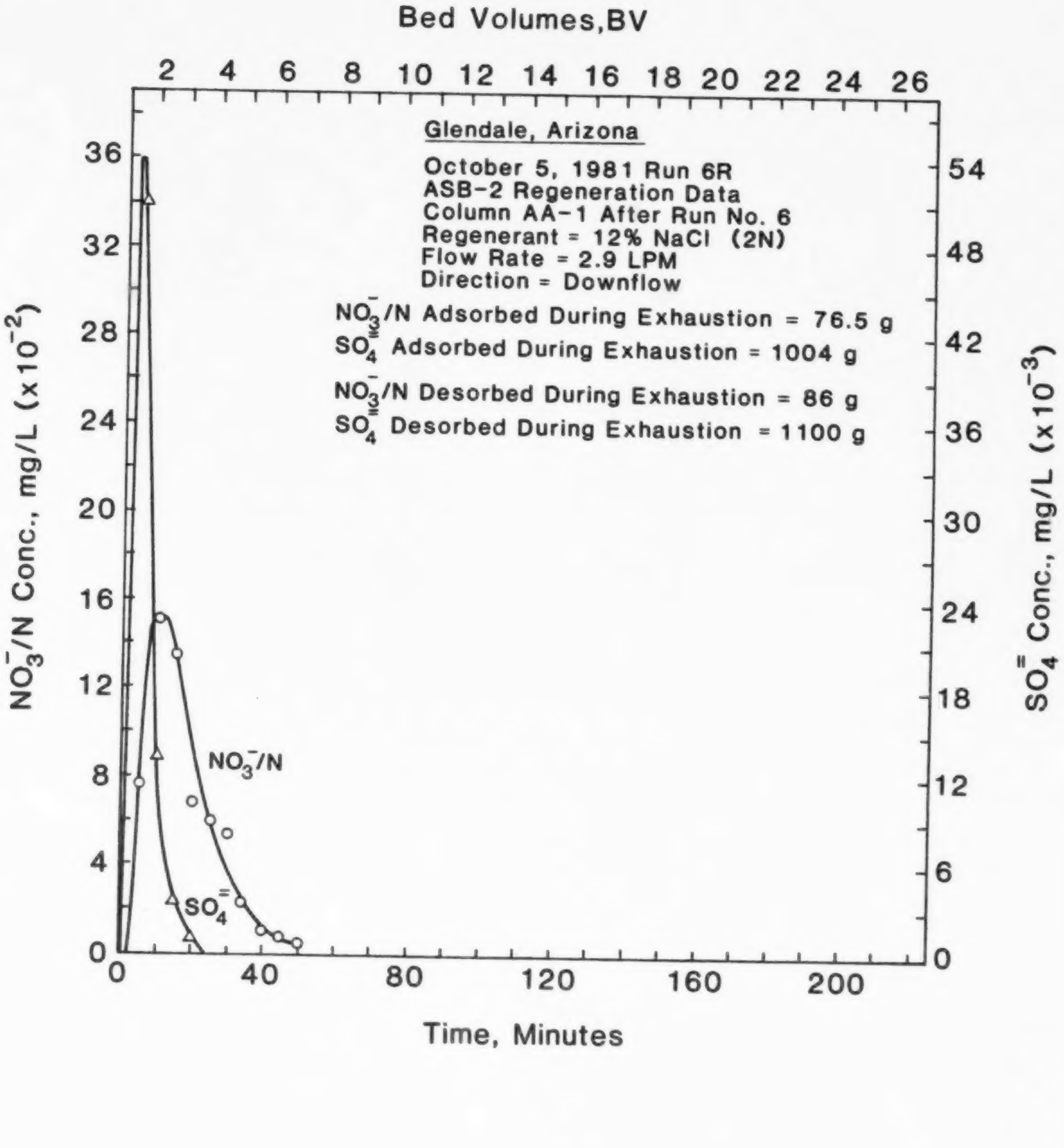


Figure C-6R. Complete regeneration Run No. 6R using 2.0 N NaCl.

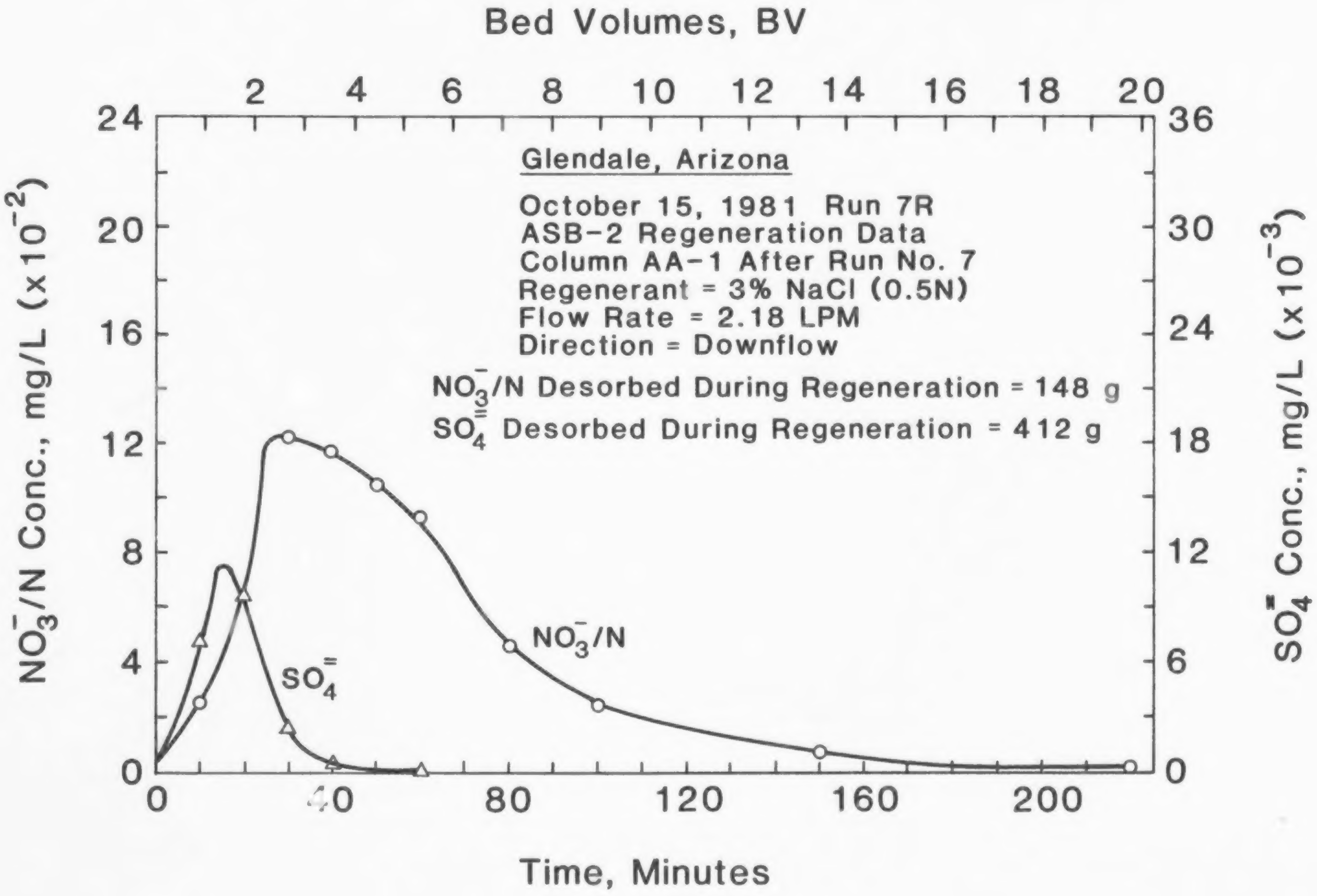


Figure C-7R. Complete regeneration Run No. 7R using 0.5 N NaCl.

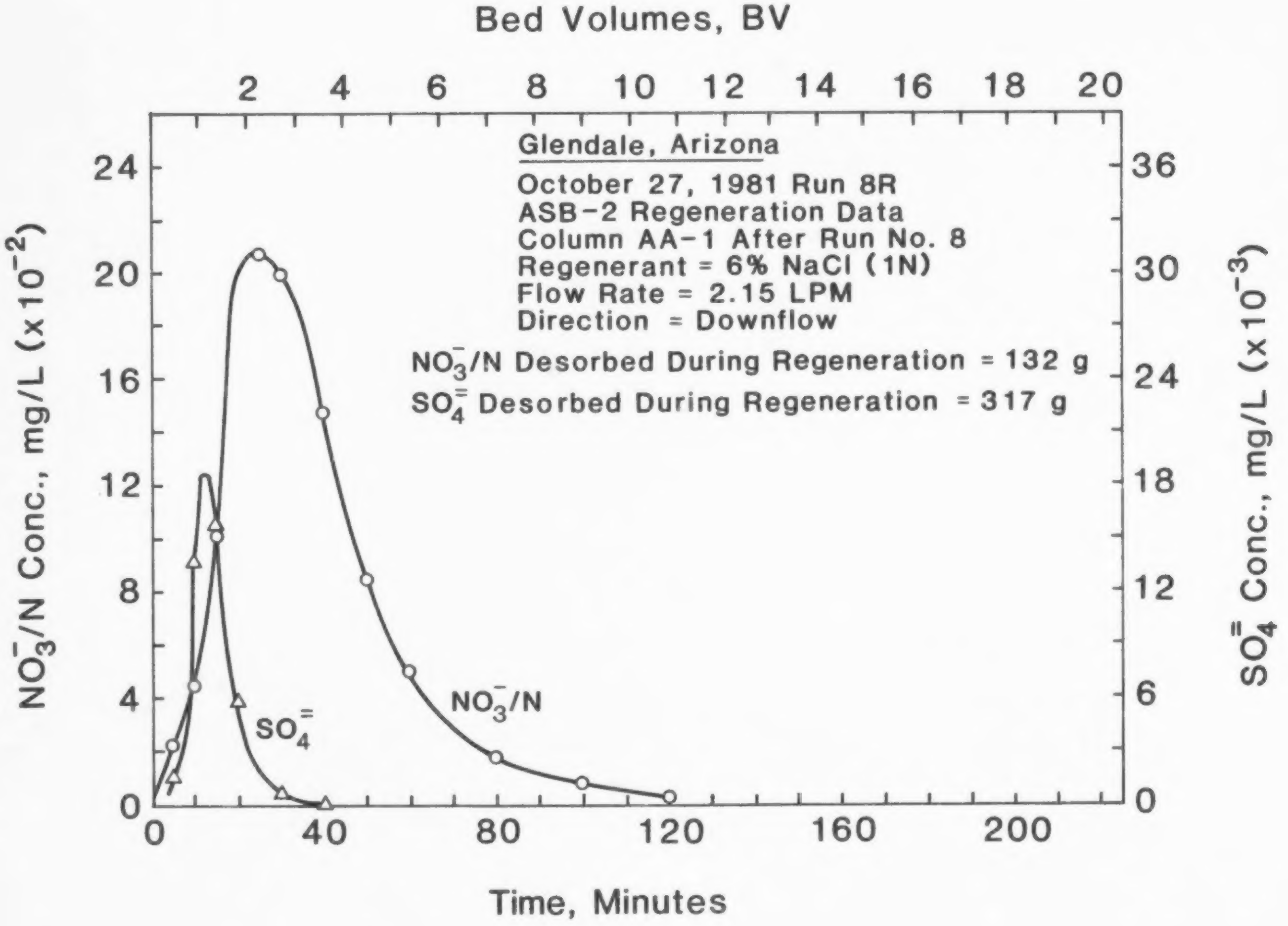


Figure C-8R. Complete regeneration Run No. 8R using 1.0 N NaCl.

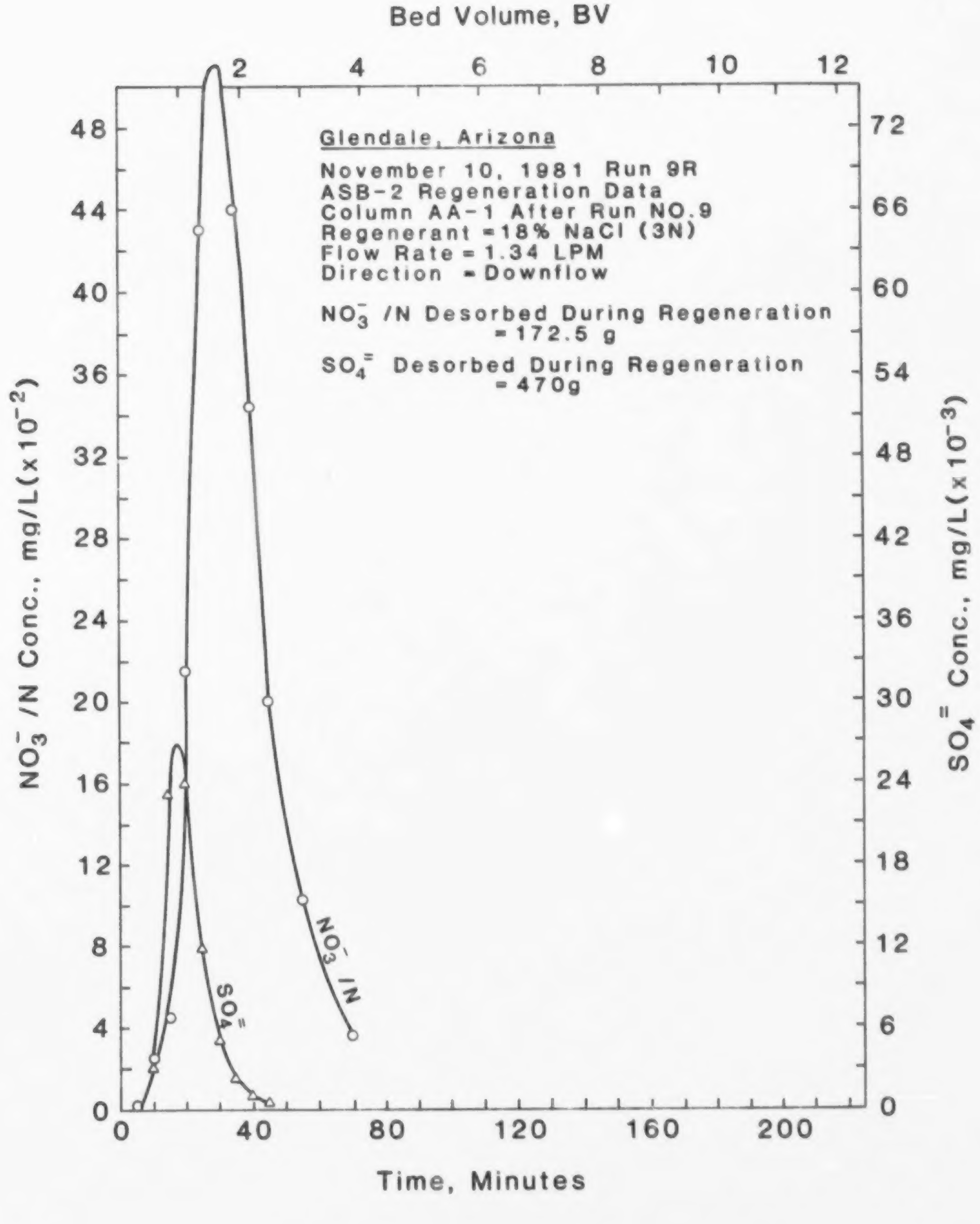


Figure C-9R. Complete regeneration Run No. 9R using 3.0 N NaCl.

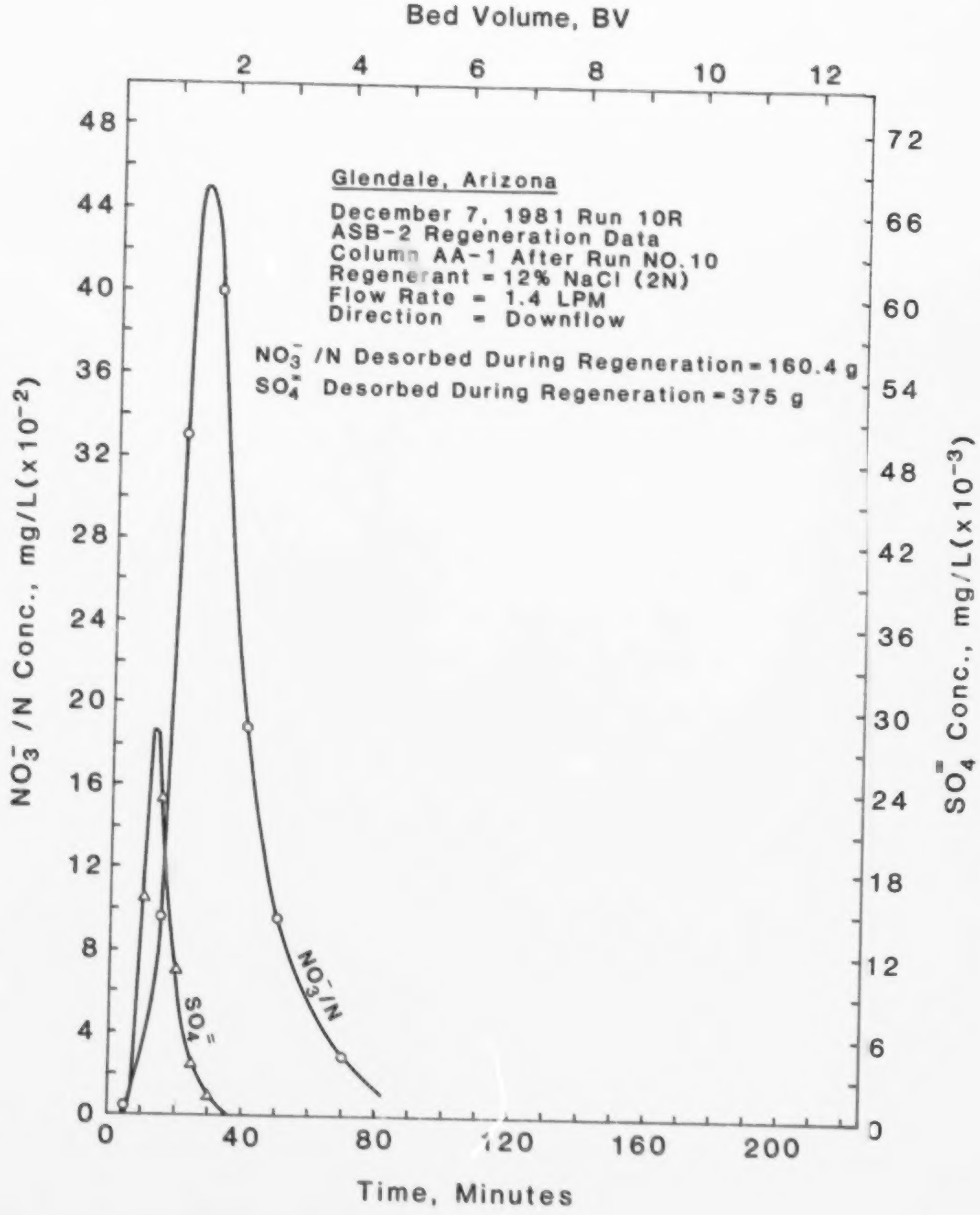


Figure C-10R. Complete regeneration Run No. 10R, using 2.0 N NaCl.

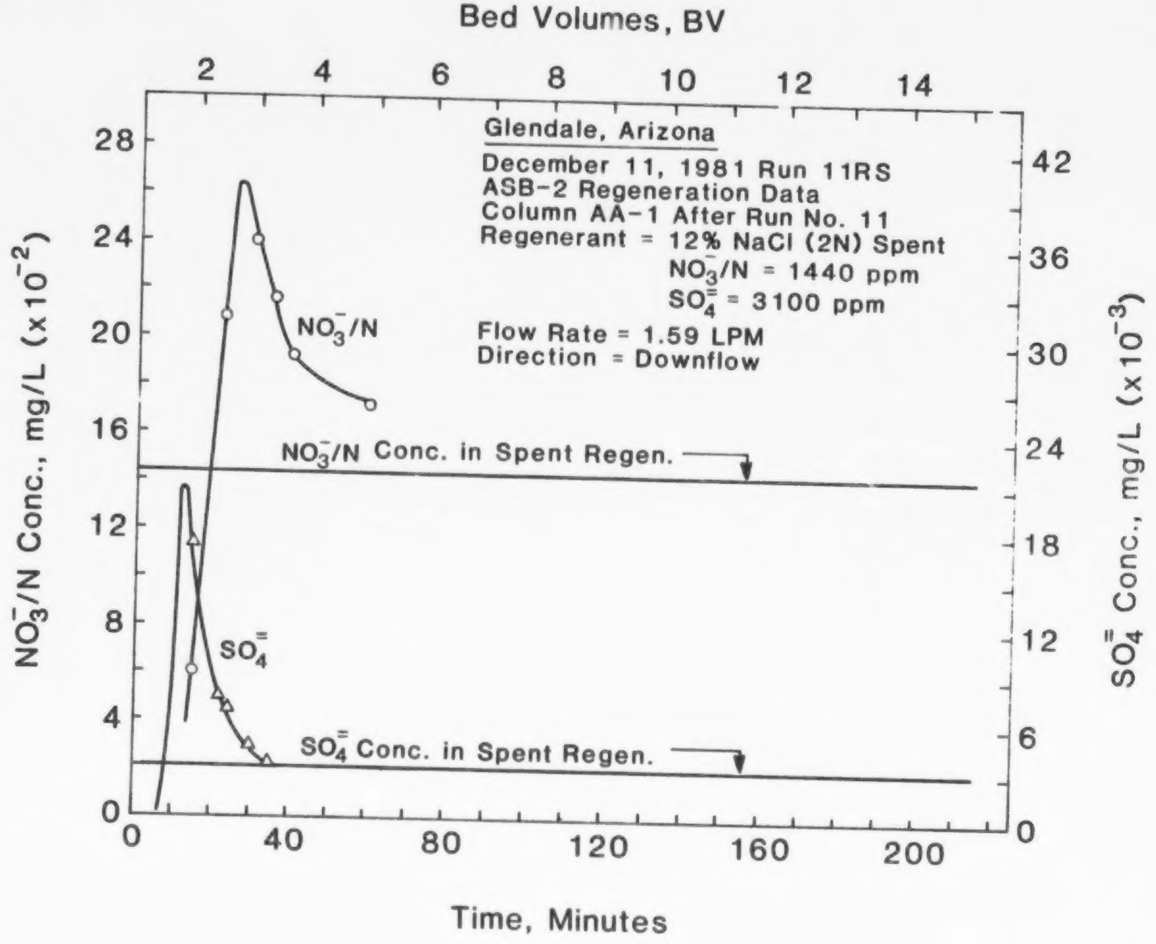


Figure C-11RS. Regeneration Run No. 11RS with spent 2.0 N NaCl regenerant from Run 10R.

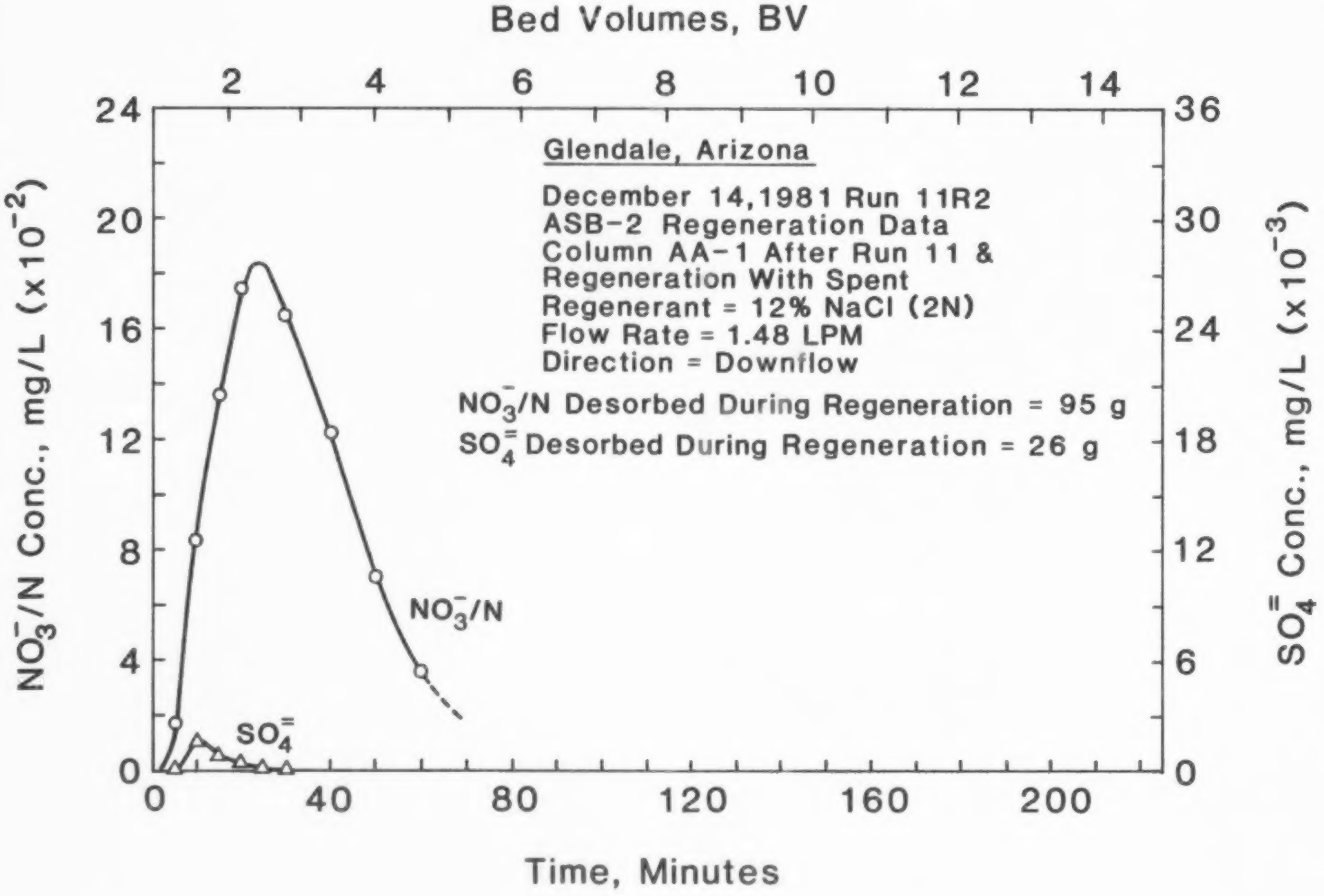


Figure C-11R2. Polishing regeneration Run No. 11R2 with 2.0 N NaCl spent regenerant (Run 11RS).

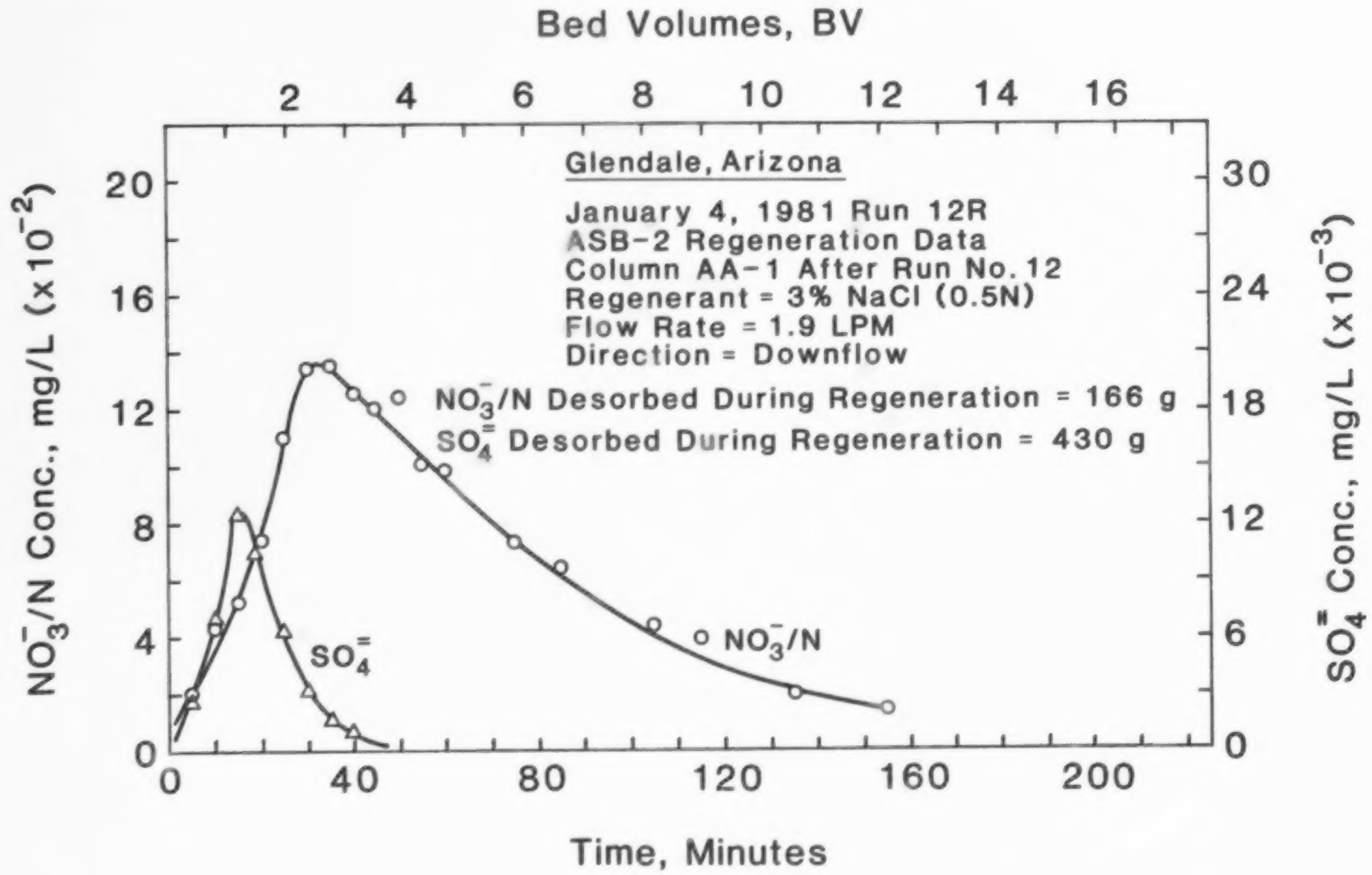


Figure C-12R. Complete regeneration Run No. 12R using 0.5 N NaCl.

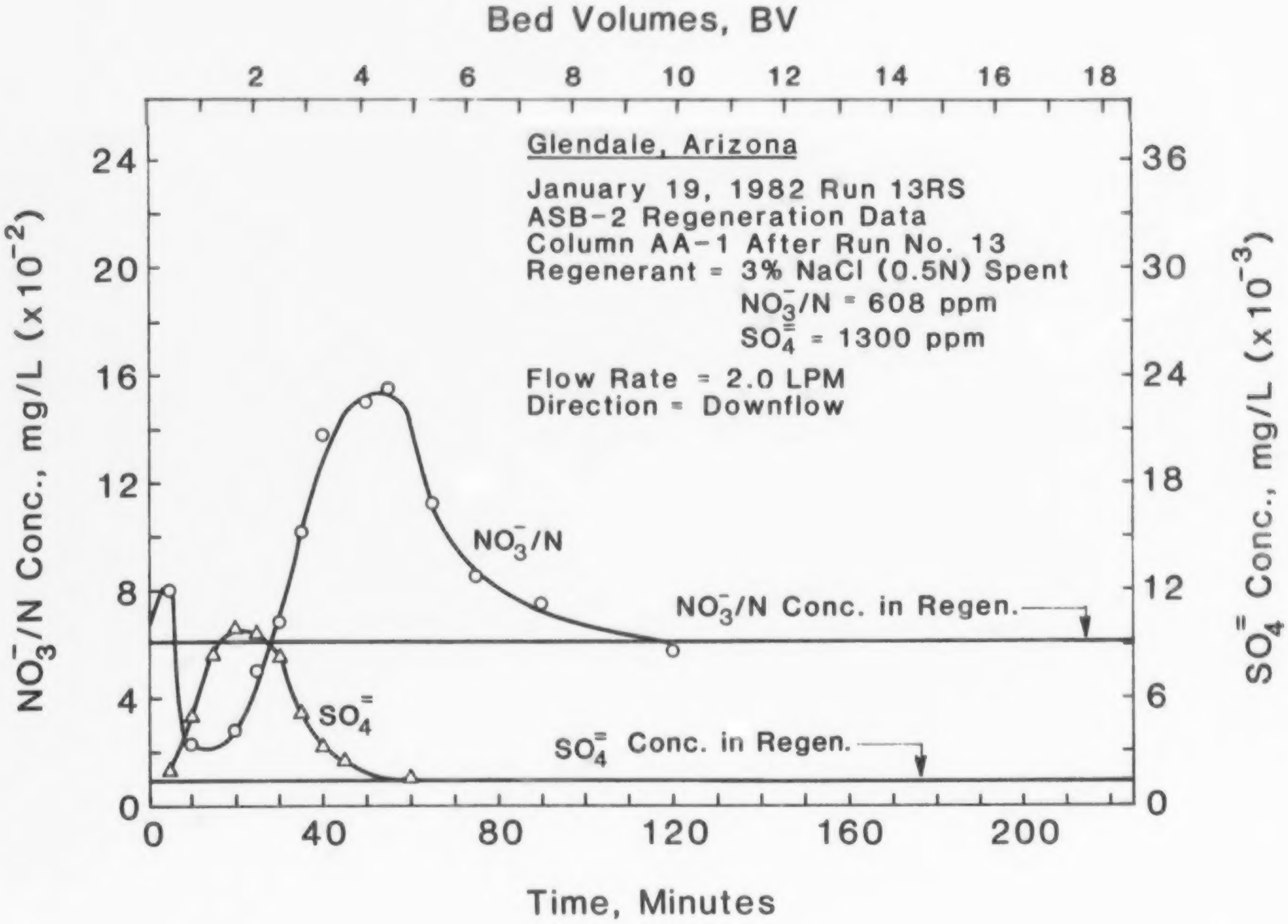


Figure C-13RS. Regeneration Run No. 13RS with spent 0.5 N regenerant from Run 12R.

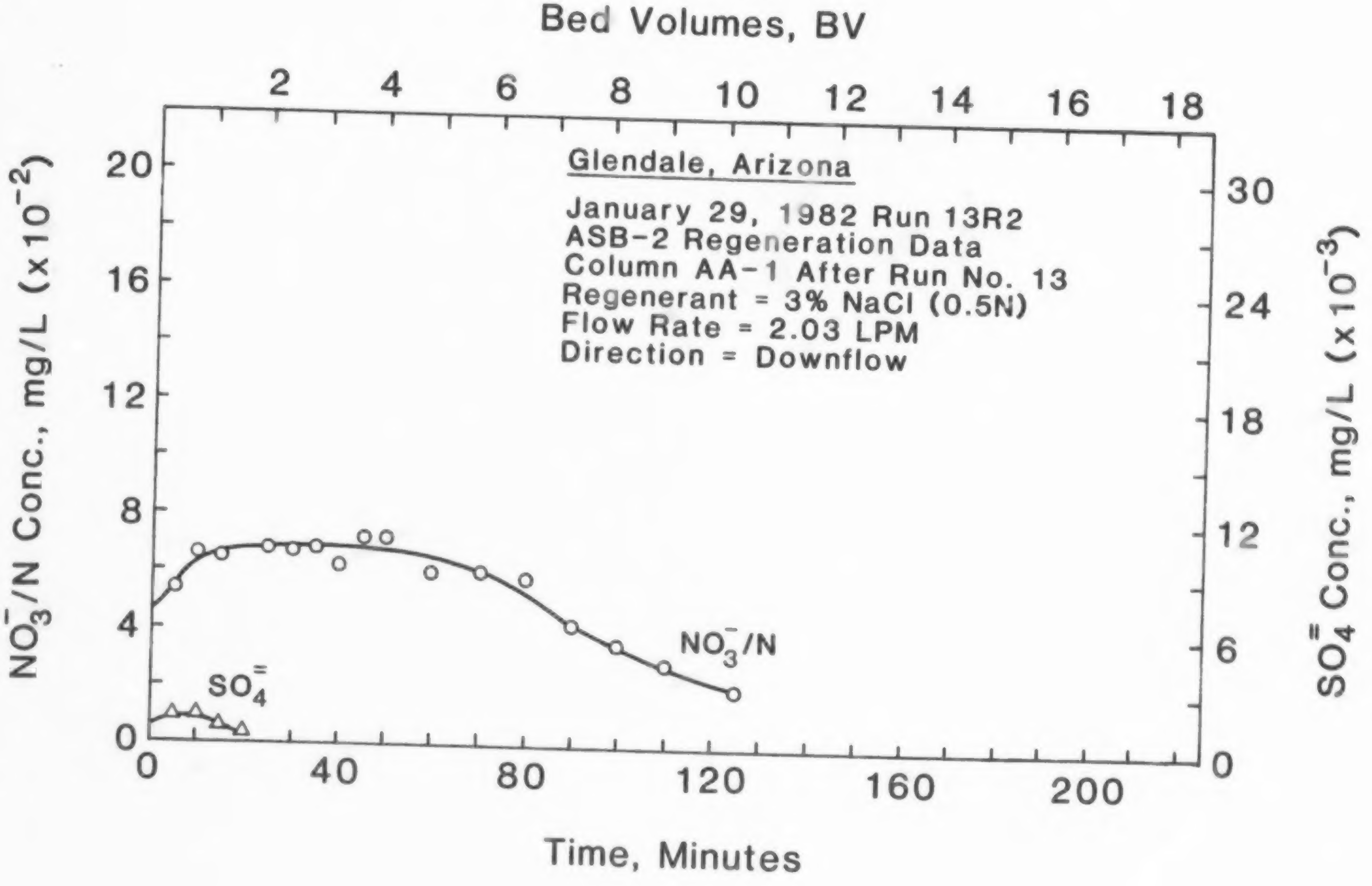


Figure C-13R2. Polishing regeneration Run No. 13R2 with 0.5 N NaCl following regeneration with spent regeneration (Run 13RS).

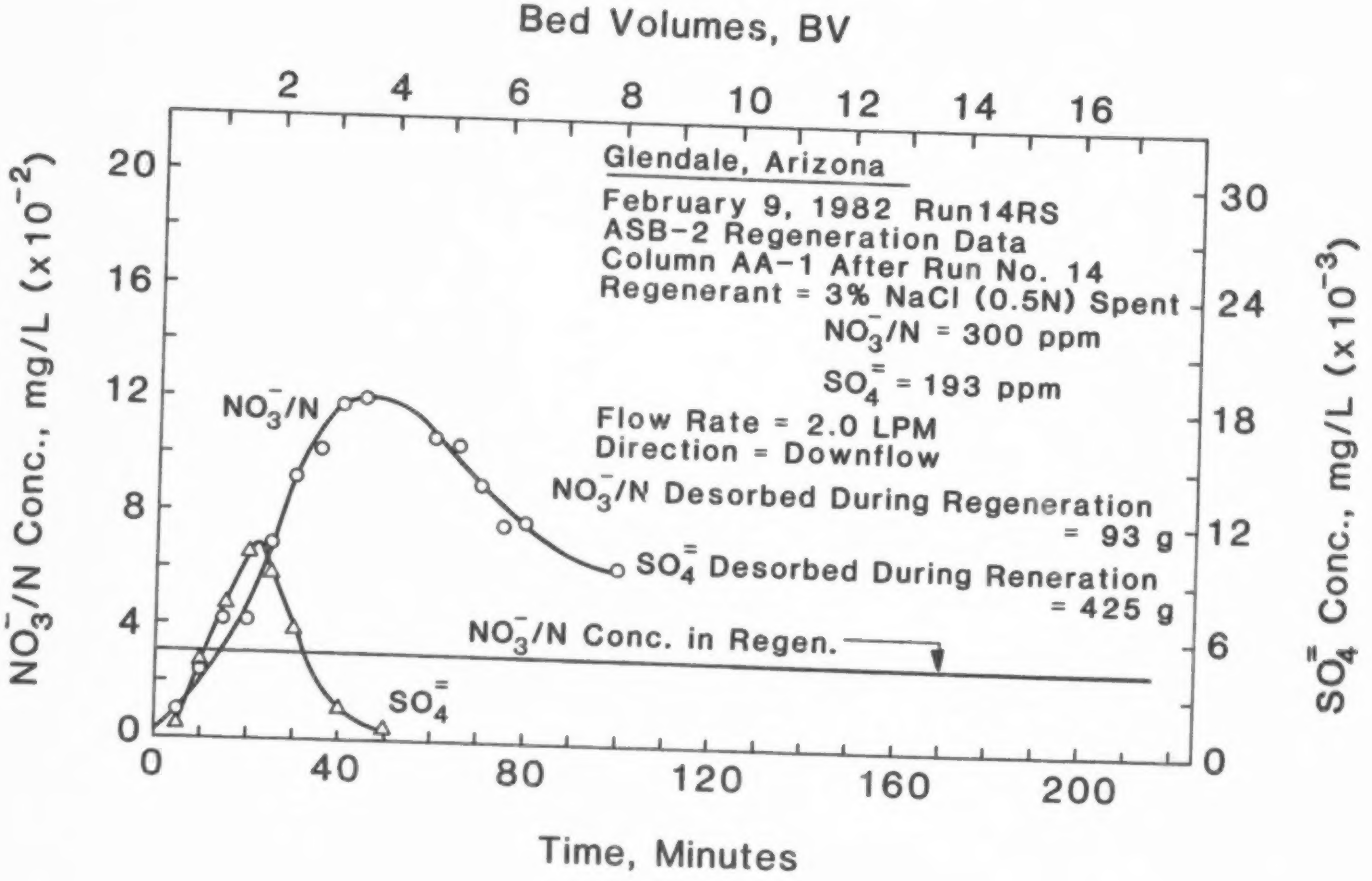


Figure C-14RS. Regeneration Run No. 14RS with spent 0.5 N regenerant from polishing regeneration Run 13RS.

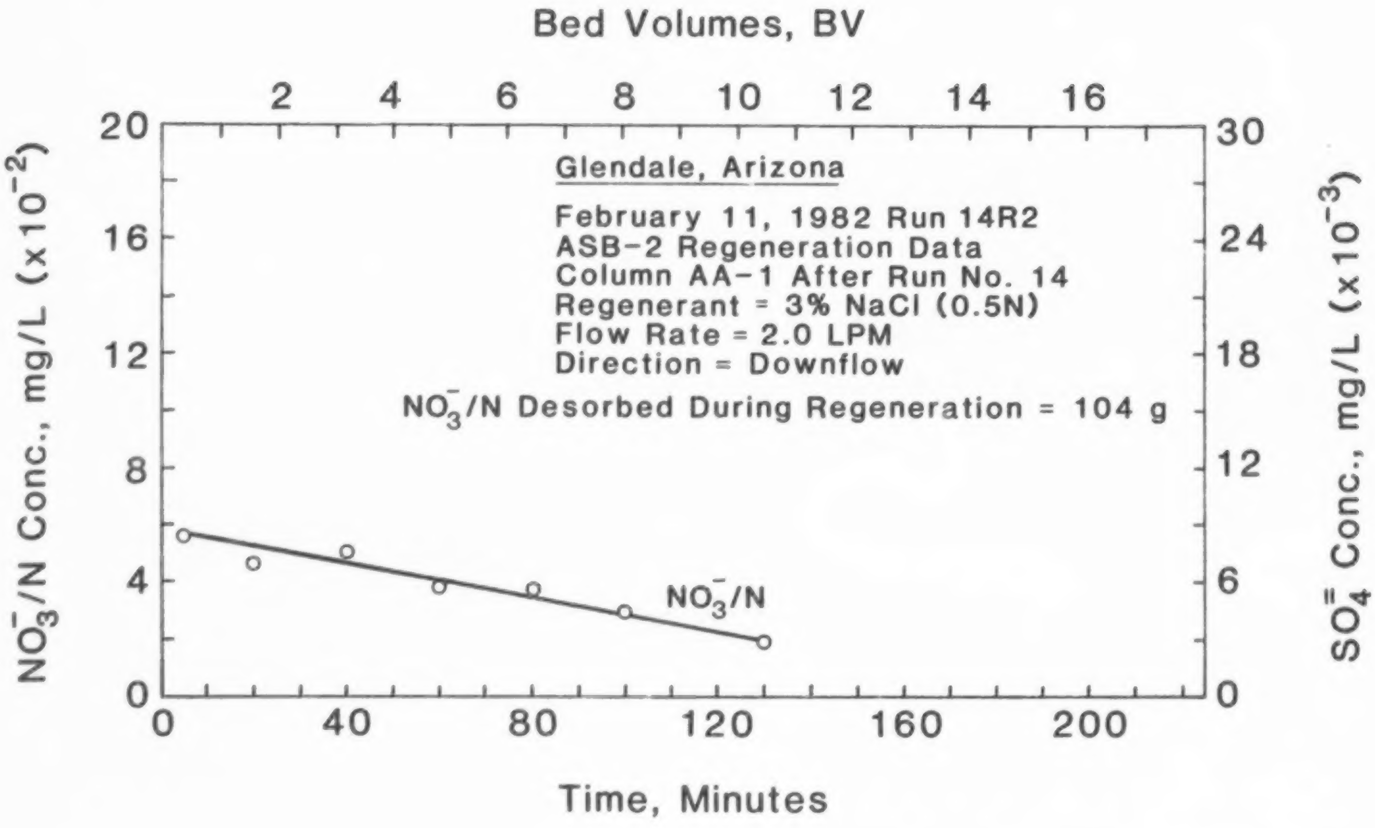


Figure C-14R2. Polishing regeneration Run No. 14R2 with 0.5 N NaCl following regeneration with spent regenerant (Run 14RS).

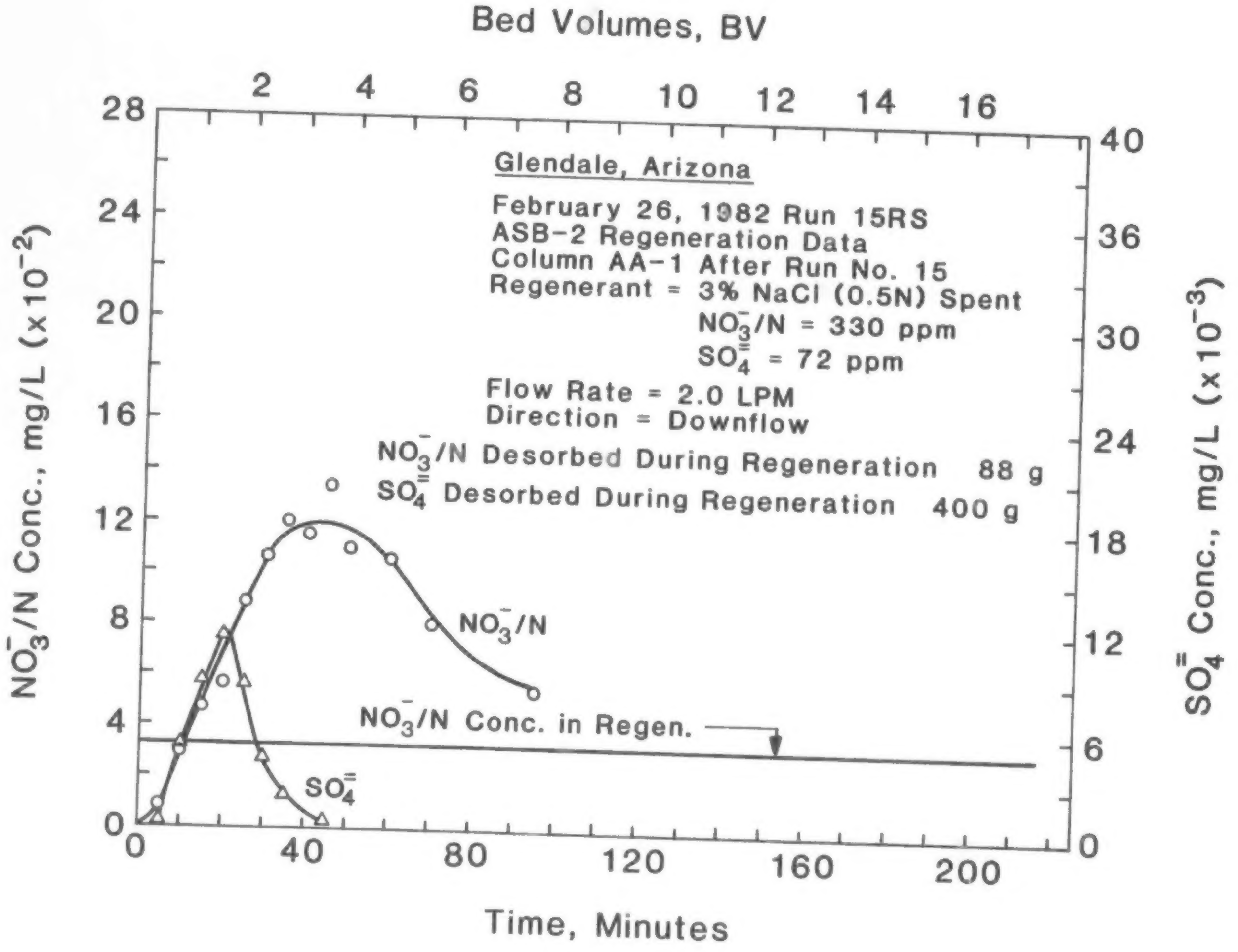


Figure C-15RS. Regeneration Run No. 15RS using spent 0.5 N regenerant from polishing regeneration Run 14R2.

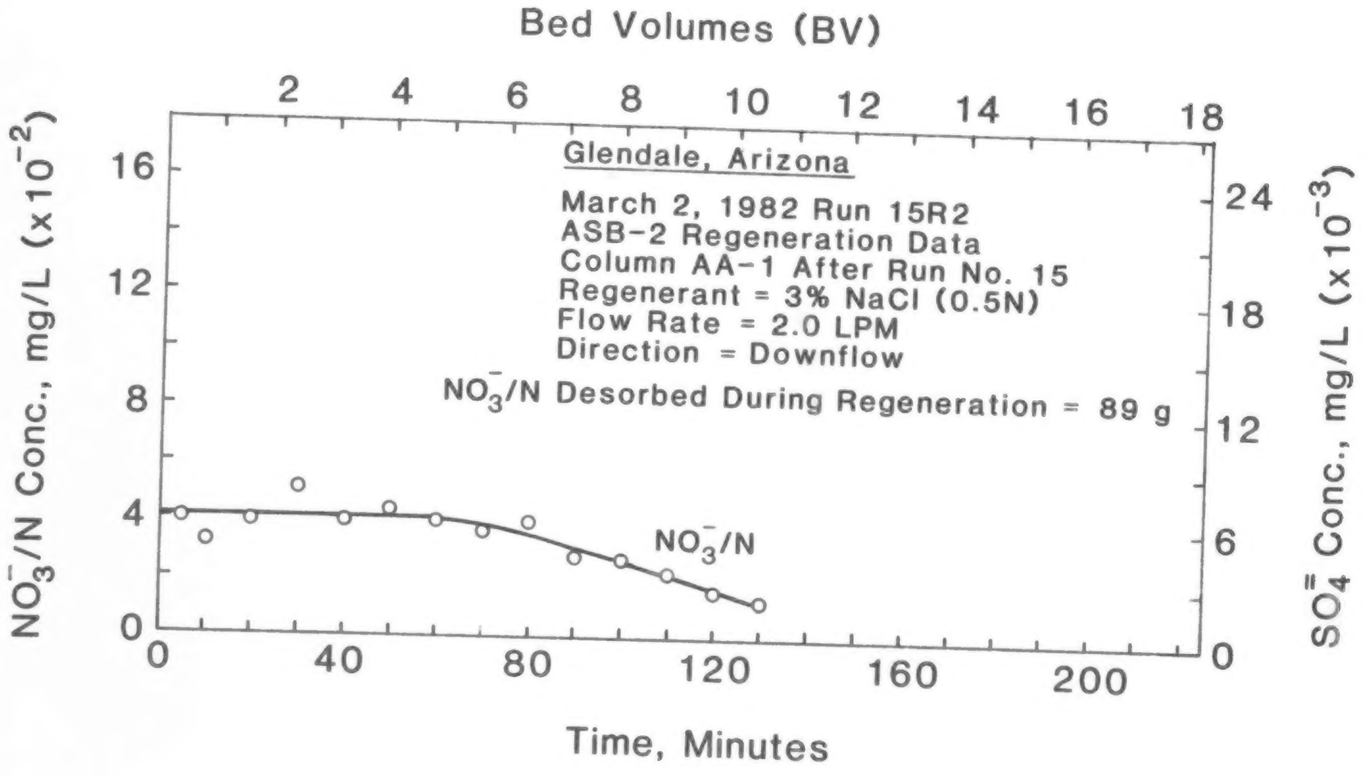


Figure C-15R2. Polishing Regeneration Run No. 15R2 using 0.5 N NaCl following regeneration with spent 0.5 N NaCl (Run 15RS).

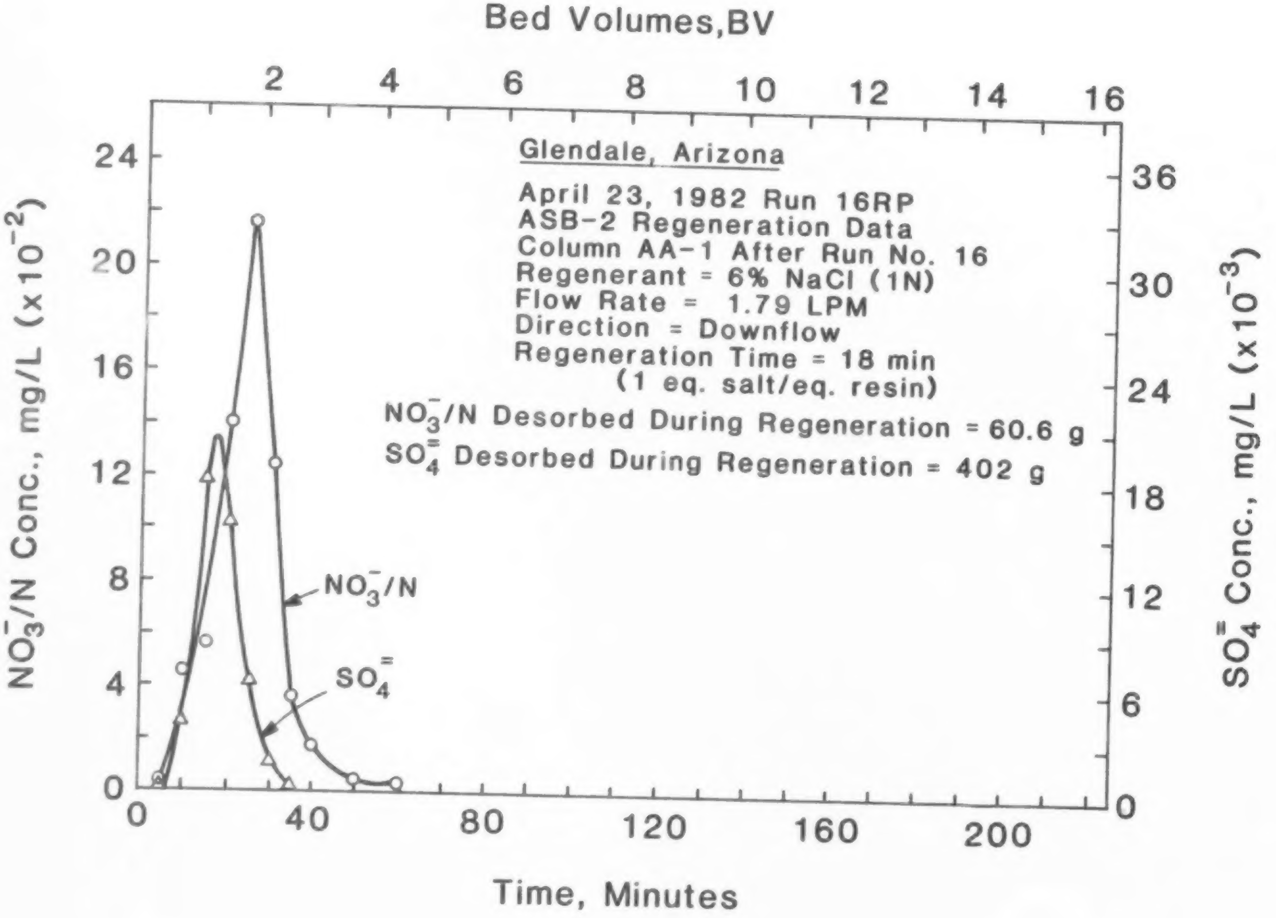


Figure C-16RP. Partial regeneration Run No. 16RP using 1.0 N NaCl at 1.0 equiv. chloride/equiv. resin.

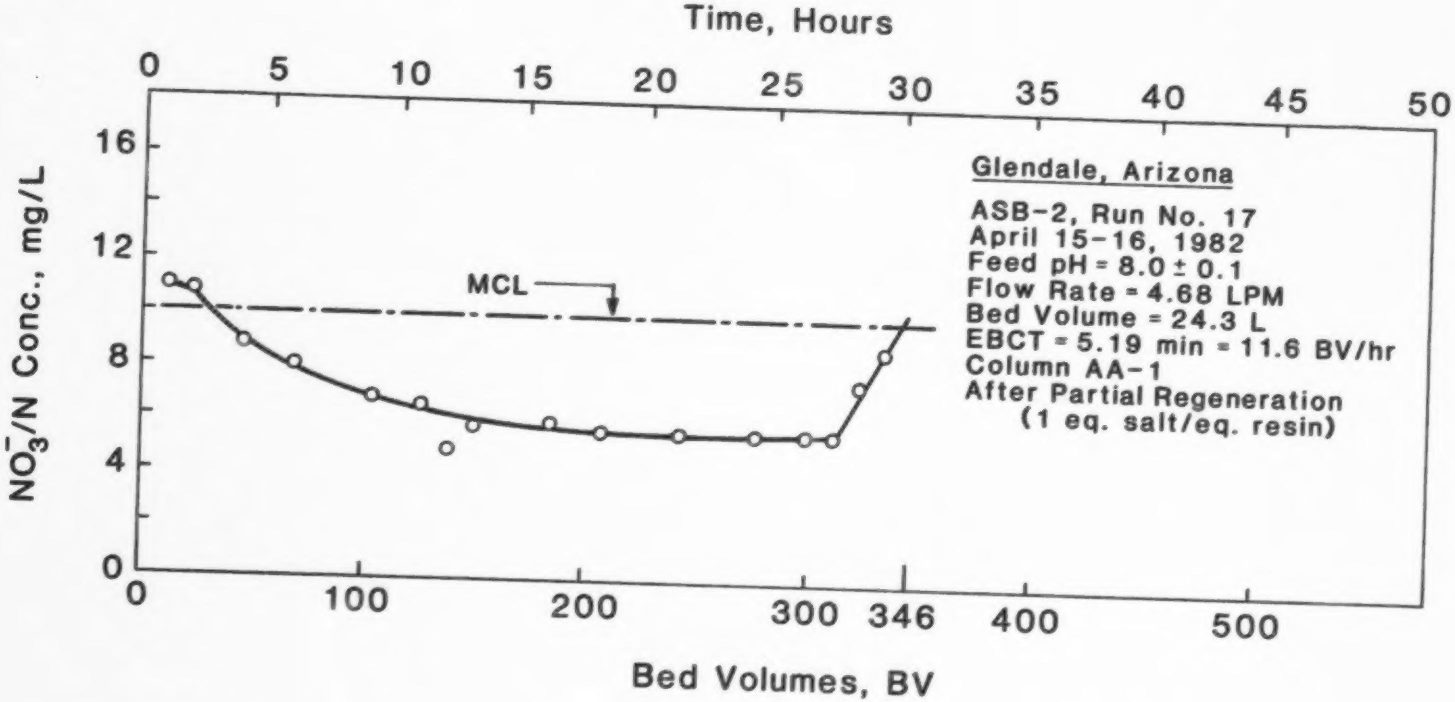


Figure C-17. Exhaustion Run No. 17 following partial regeneration with 1.0 equiv. chloride/equiv. resin.

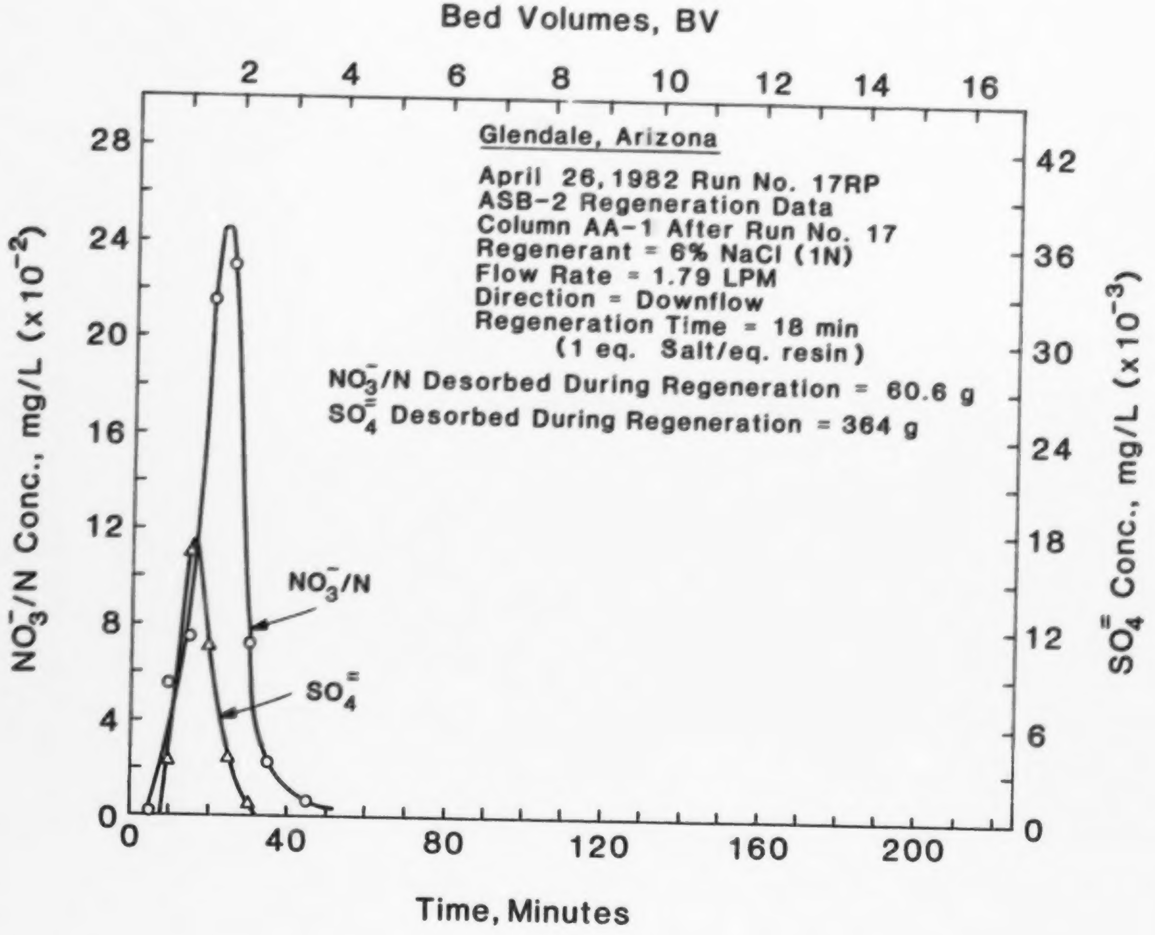


Figure C-17RP. Partial regeneration Run No. 17RP using 1.0 N NaCl at 1.0 equiv. chloride/equiv. resin.

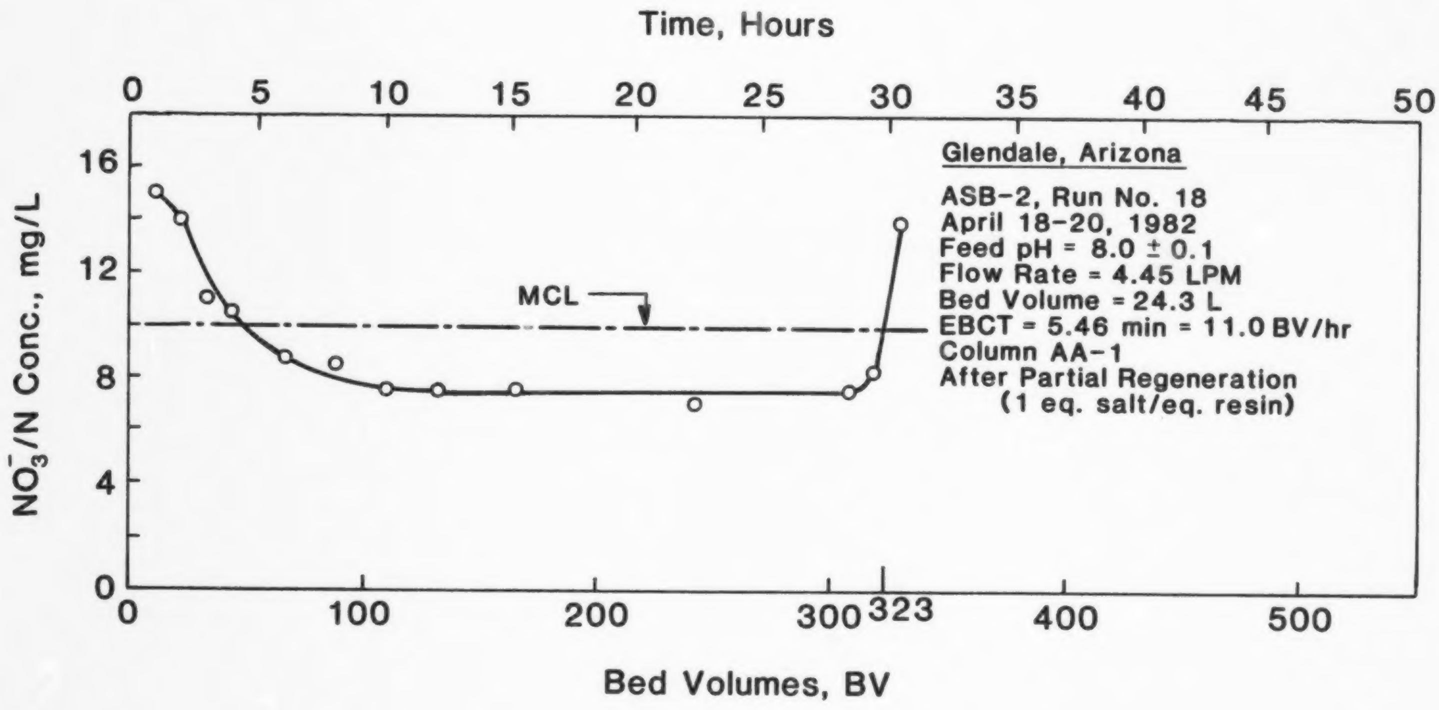


Figure C-18. Exhaustion Run No. 18 following partial regeneration with 1.0 equiv. chloride/equiv. resin.

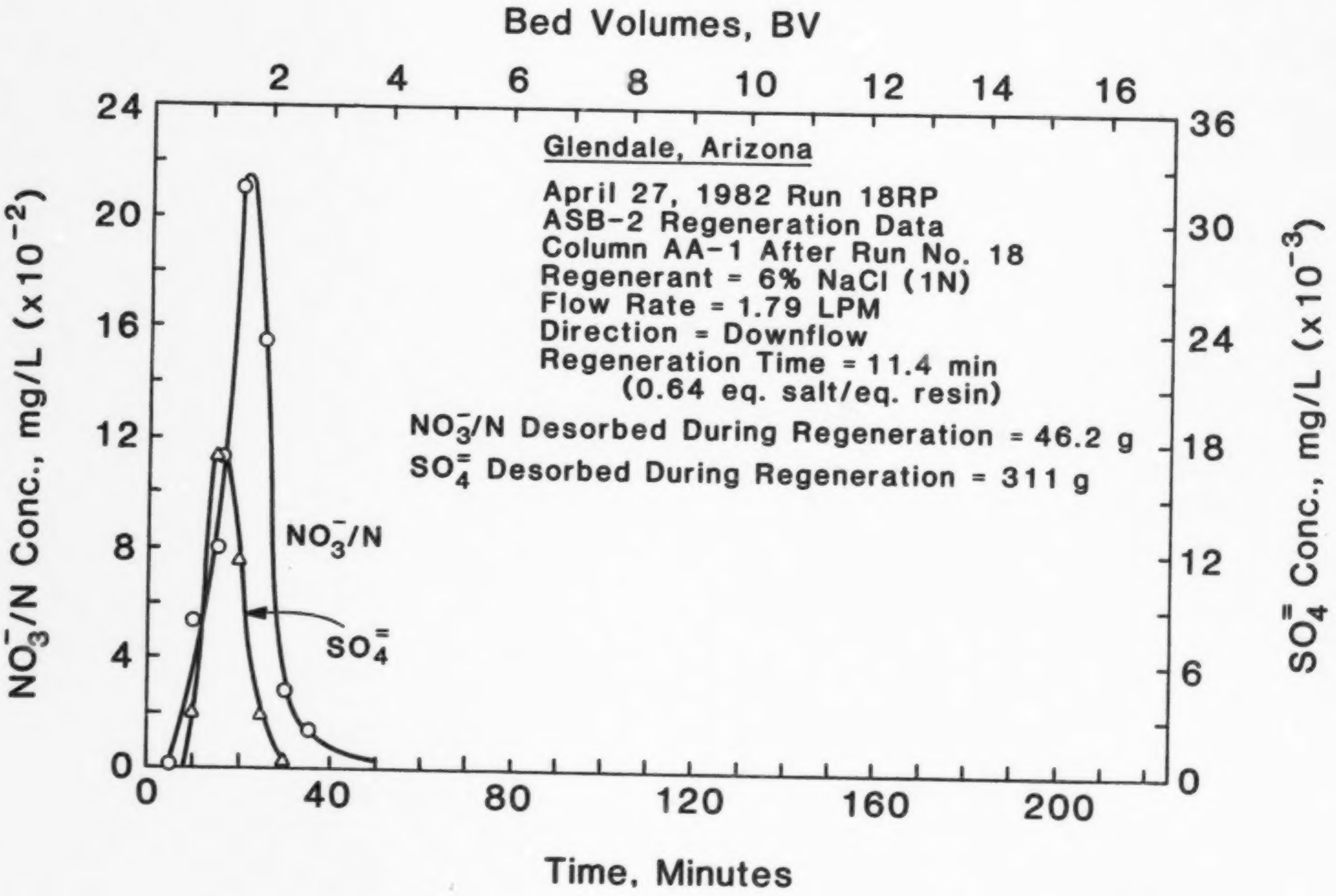


Figure C-18RP. Partial regeneration Run No. 18RP using 1.0 N NaCl at 0.64 equiv. chloride/equiv. resin.

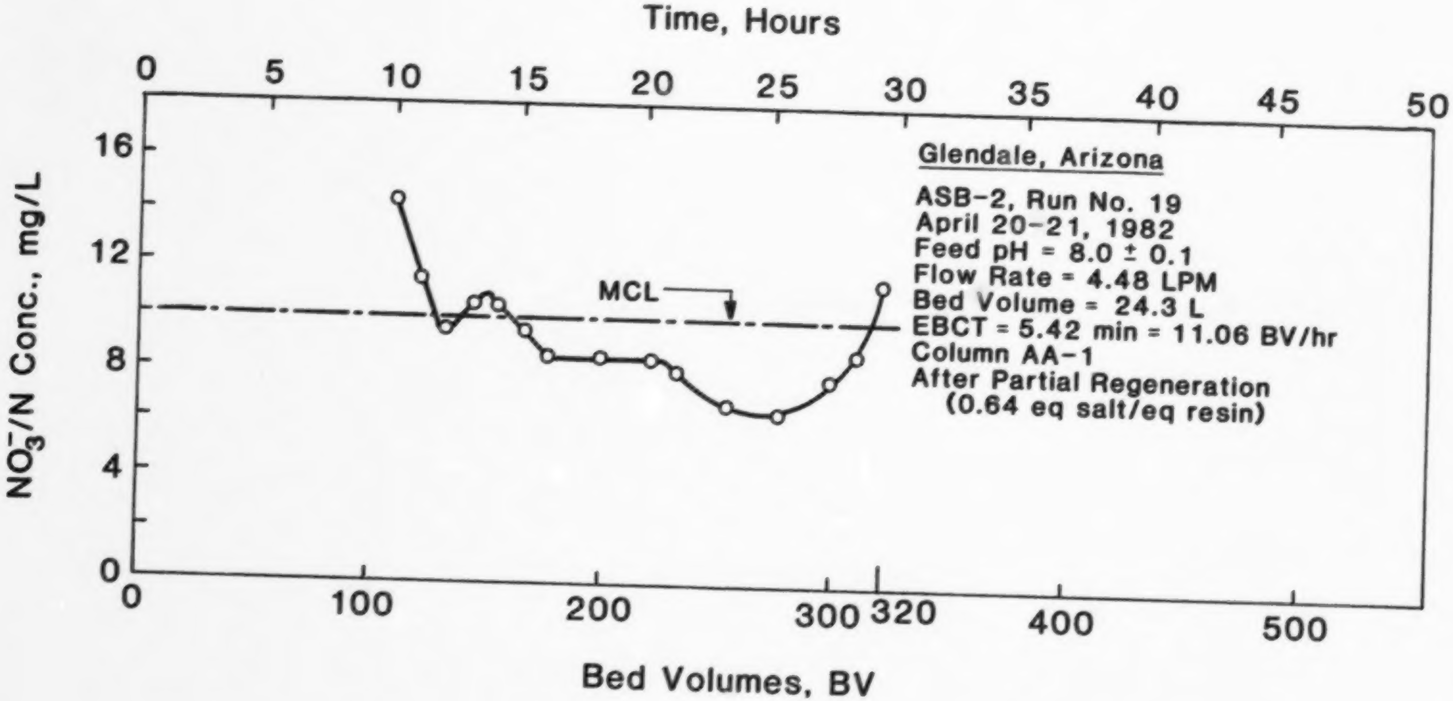


Figure C-19. Exhaustion Run No. 19 following partial regeneration with 0.64 equiv. chloride/equiv. resin.

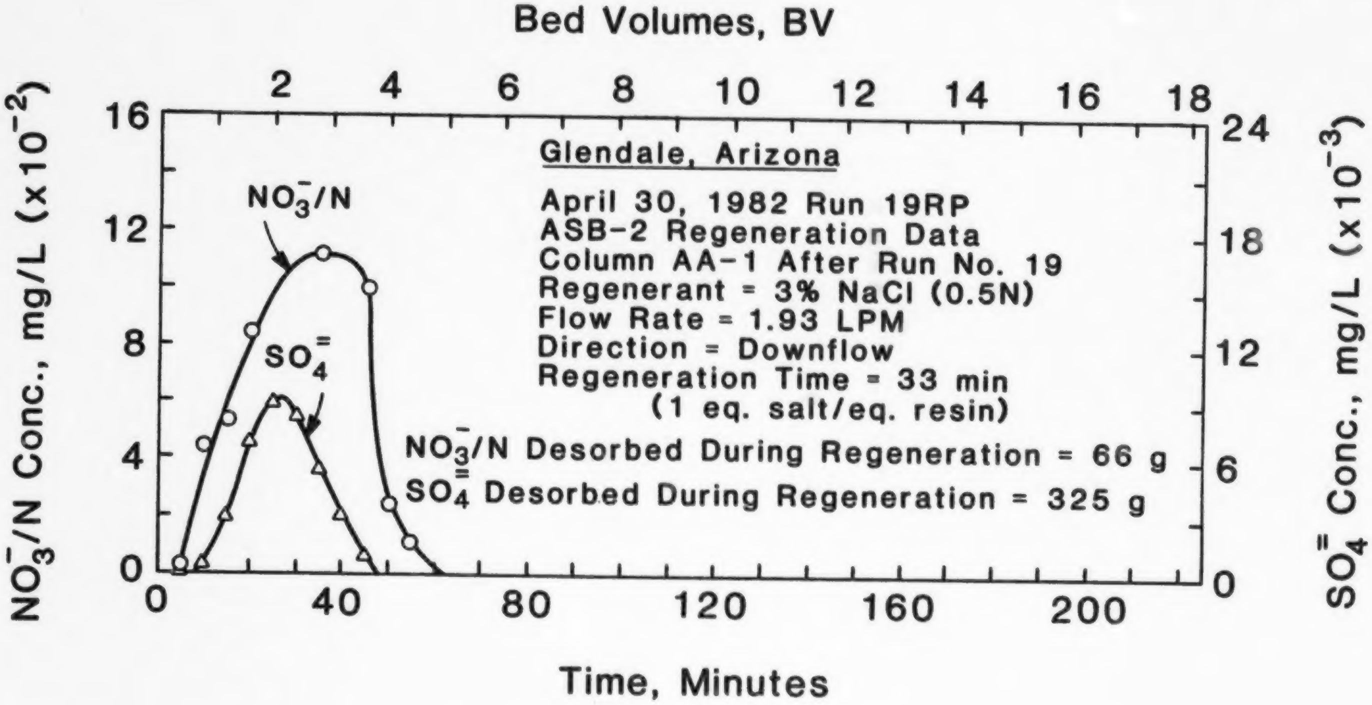


Figure C-19RP. Partial regeneration Run No. 19RP using 0.5 N NaCl at 1.0 equiv. chloride/equiv. resin.

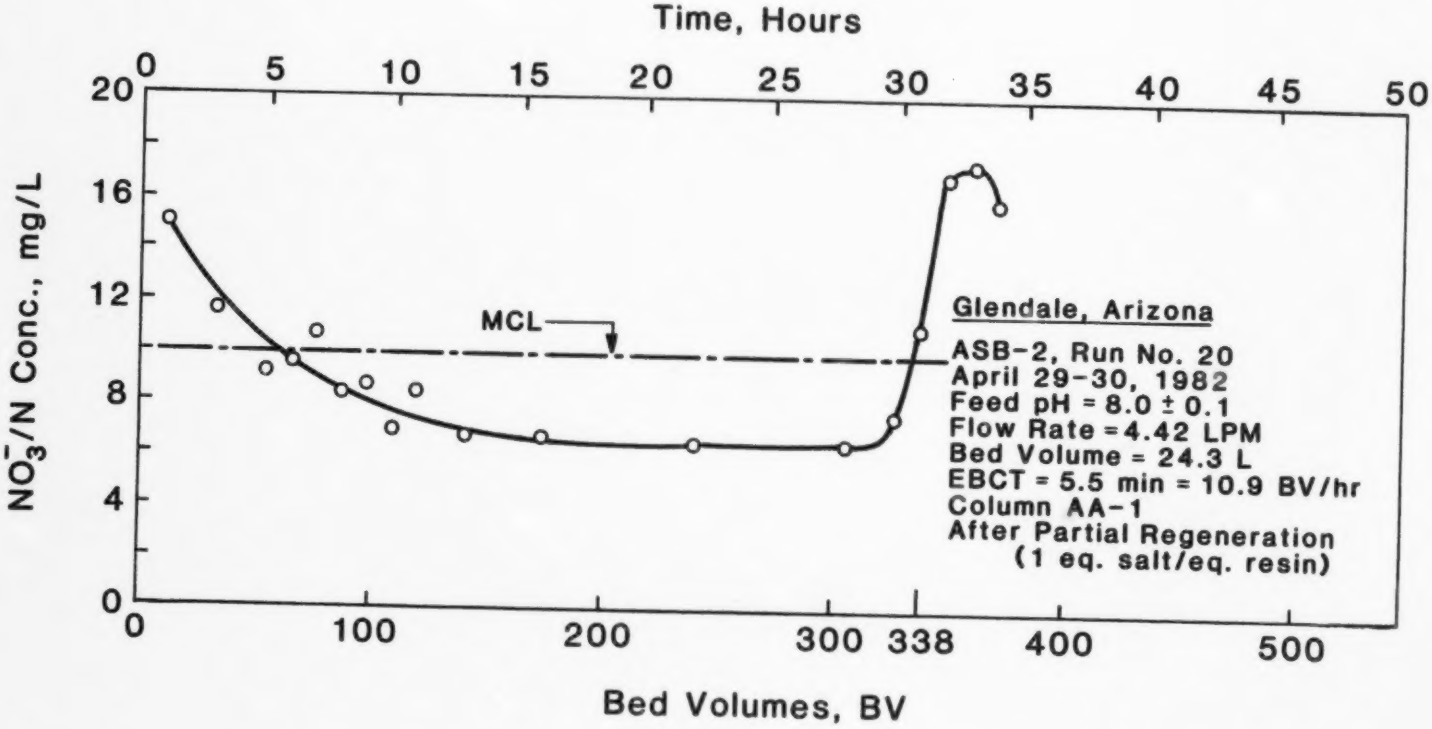


Figure C-20. Exhaustion Run No. 20 following partial regeneration with 1.0 equiv. chloride/equiv. resin.

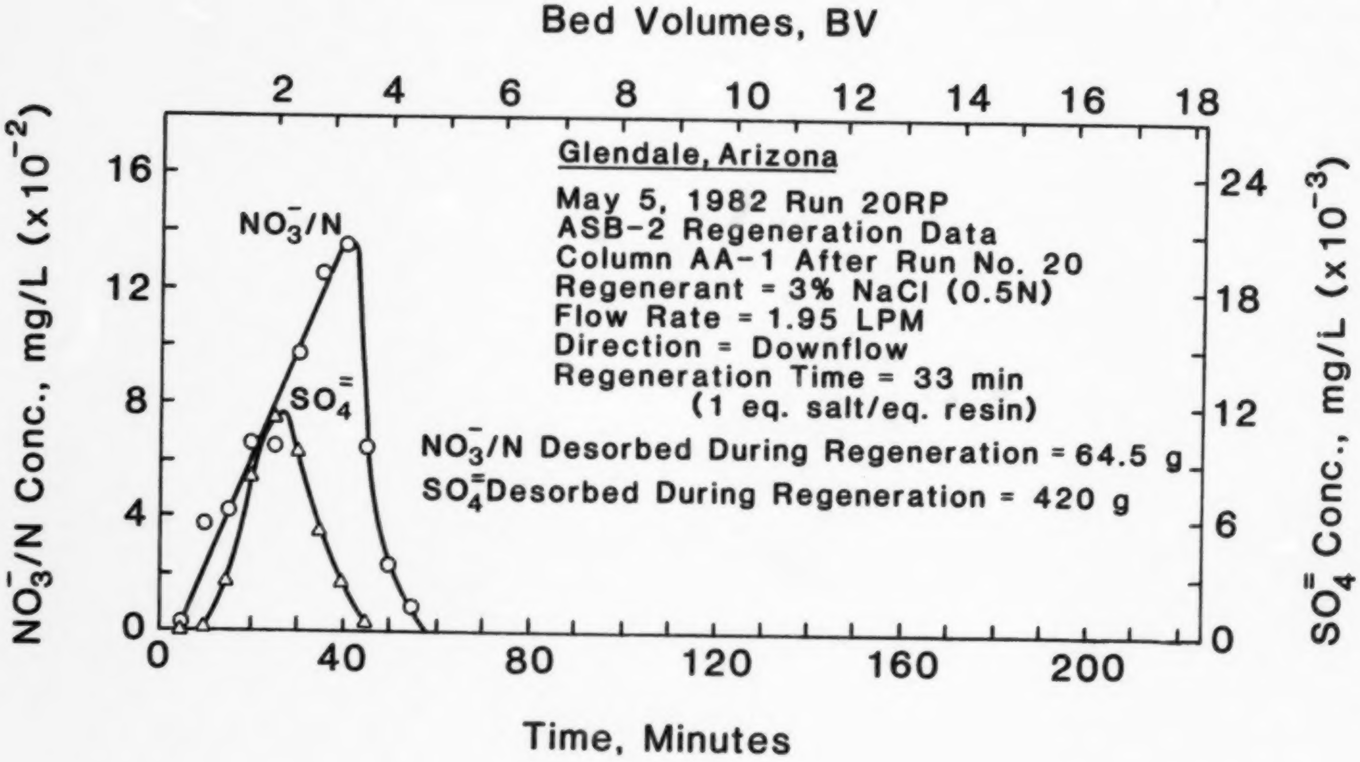


Figure C-20RP. Partial regeneration Run No. 20RP using 0.5 N NaCl at 1.0 equiv. chloride/equiv. resin.

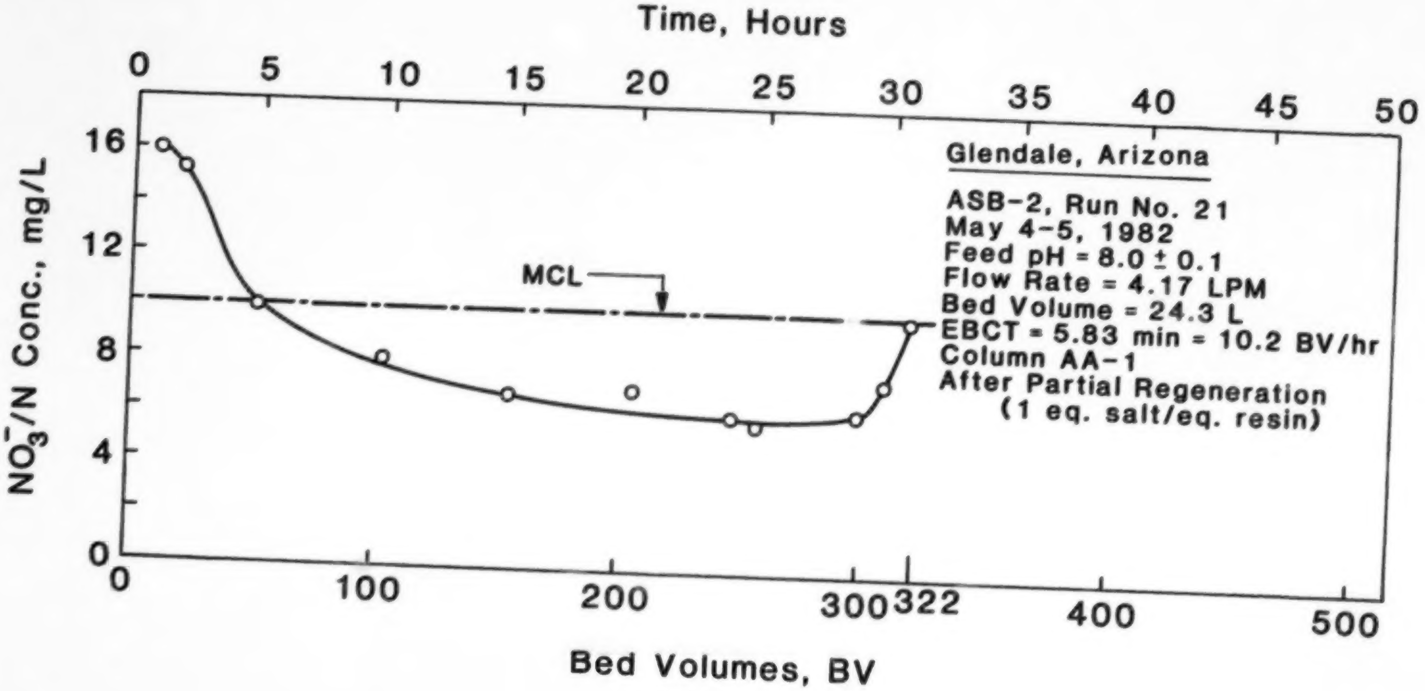


Figure C-21. Exhaustion Run No. 21 following partial regeneration with 1.0 equiv. chloride/equiv. resin.

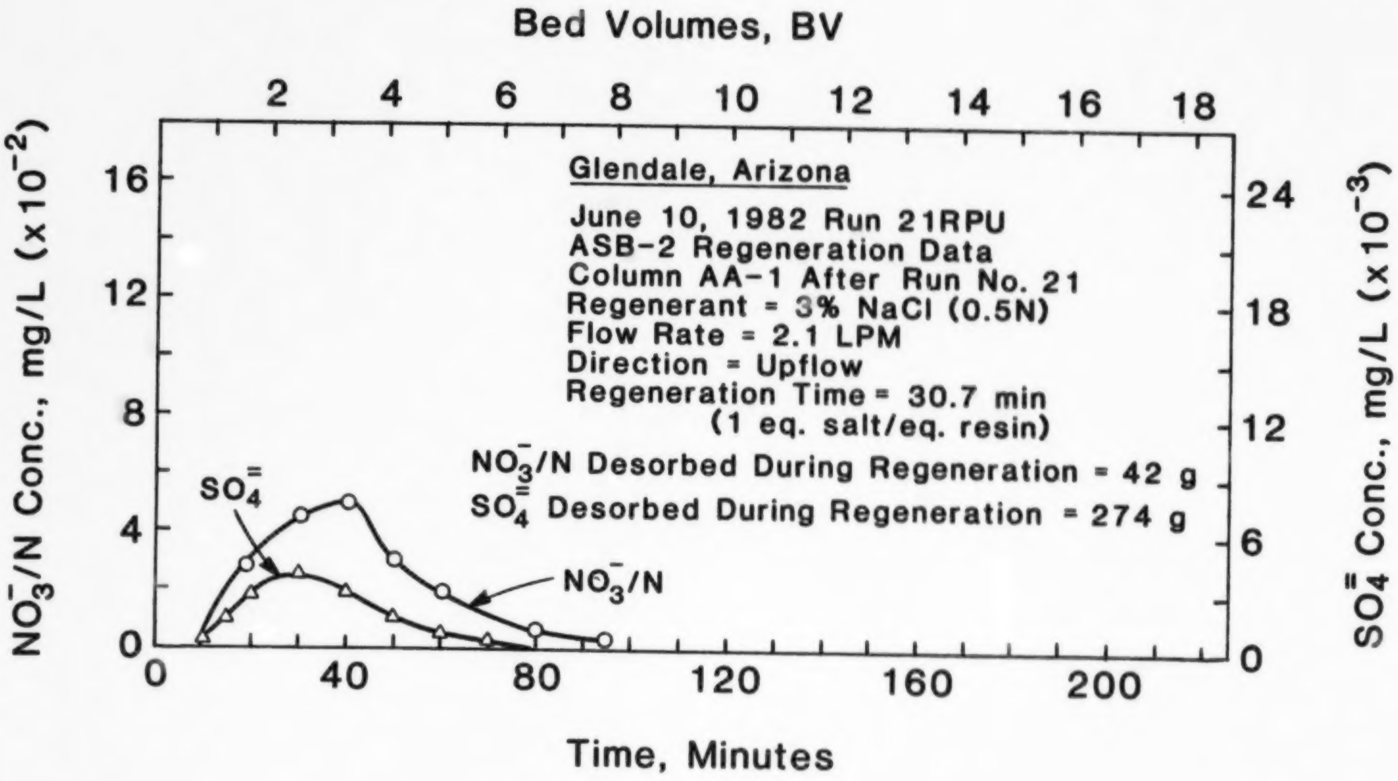


Figure C-21RP. Upflow partial regeneration Run No. 21RPI using 0.5 N at 1.0 equiv. chloride/ equiv. resin.

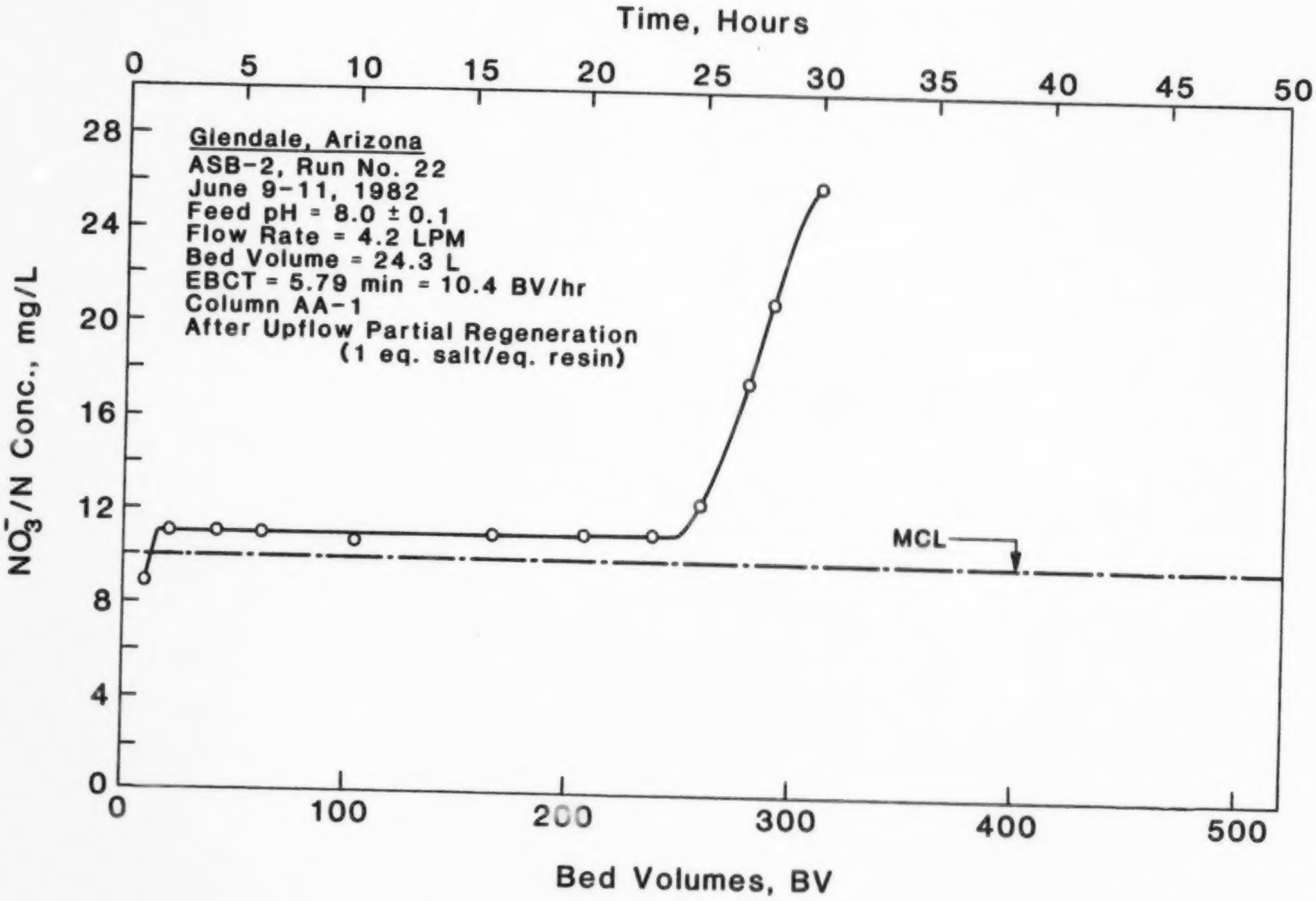


Figure C-22. Exhaustion Run No. 22 following upflow partial regeneration with 1.0 equiv. chloride/equiv. resin.

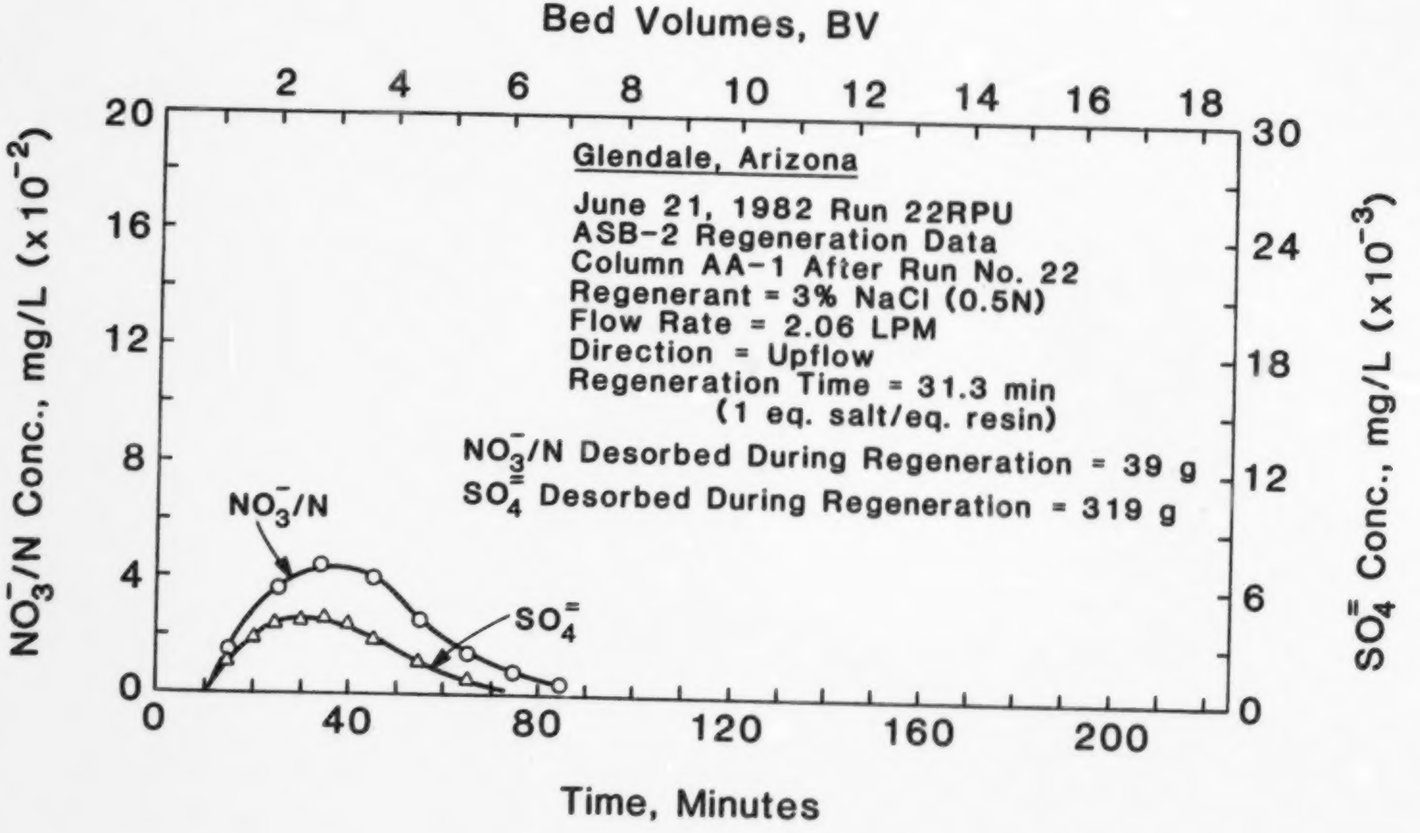


Figure C-22RPU. Upflow partial regeneration Run No. 22RPU using 0.5 N NaCl at 1.0 equiv. chloride/equiv. resin.

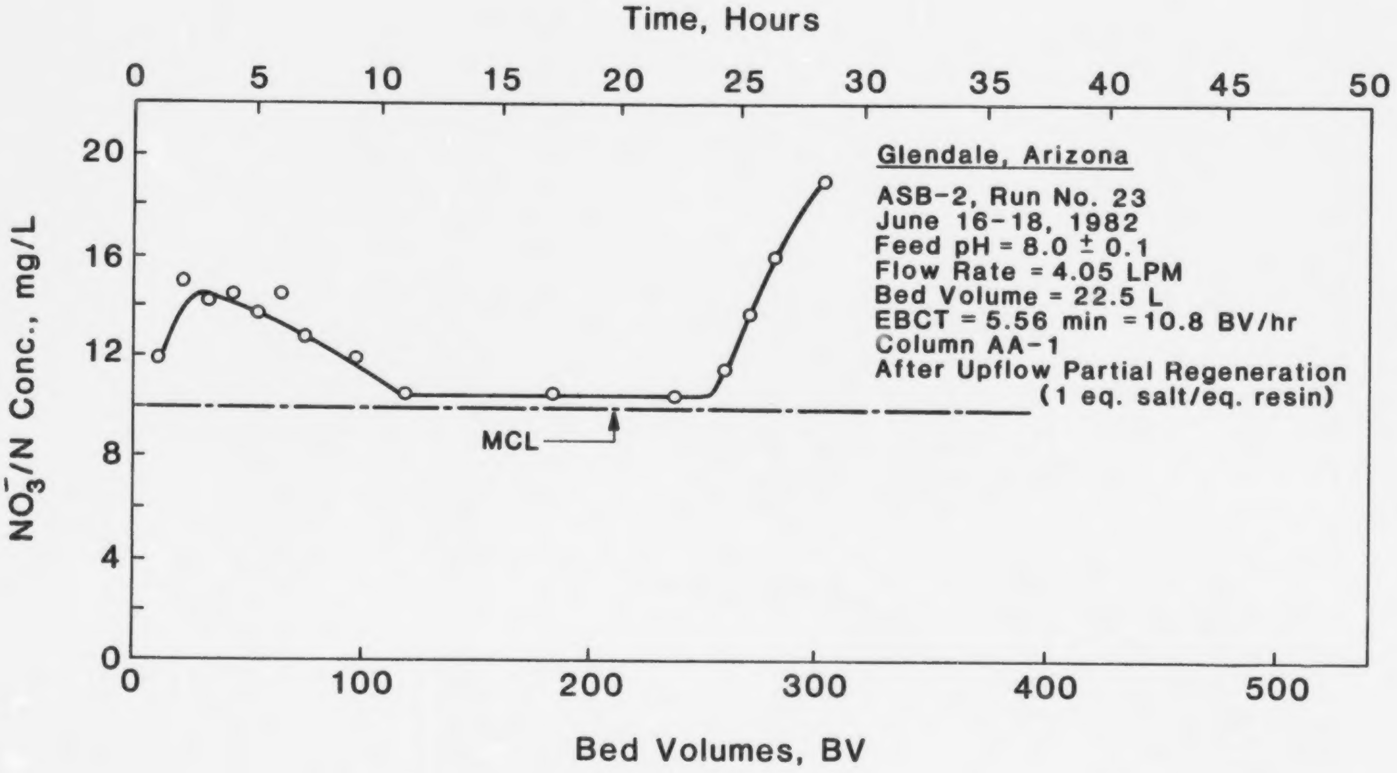


Figure C-23. Exhaustion Run No. 23 following upflow partial regeneration with 1.0 equiv. chloride/ equiv. resin.

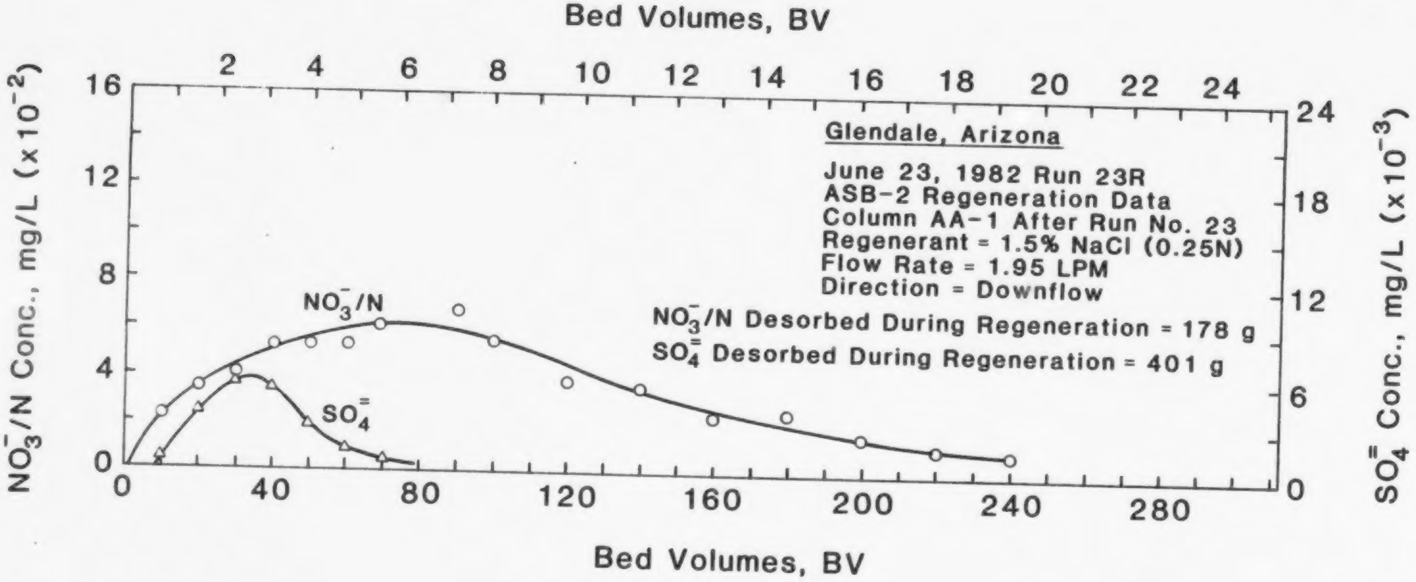


Figure C-23R. Complete regeneration Run No. 23R using 0.25 N NaCl.

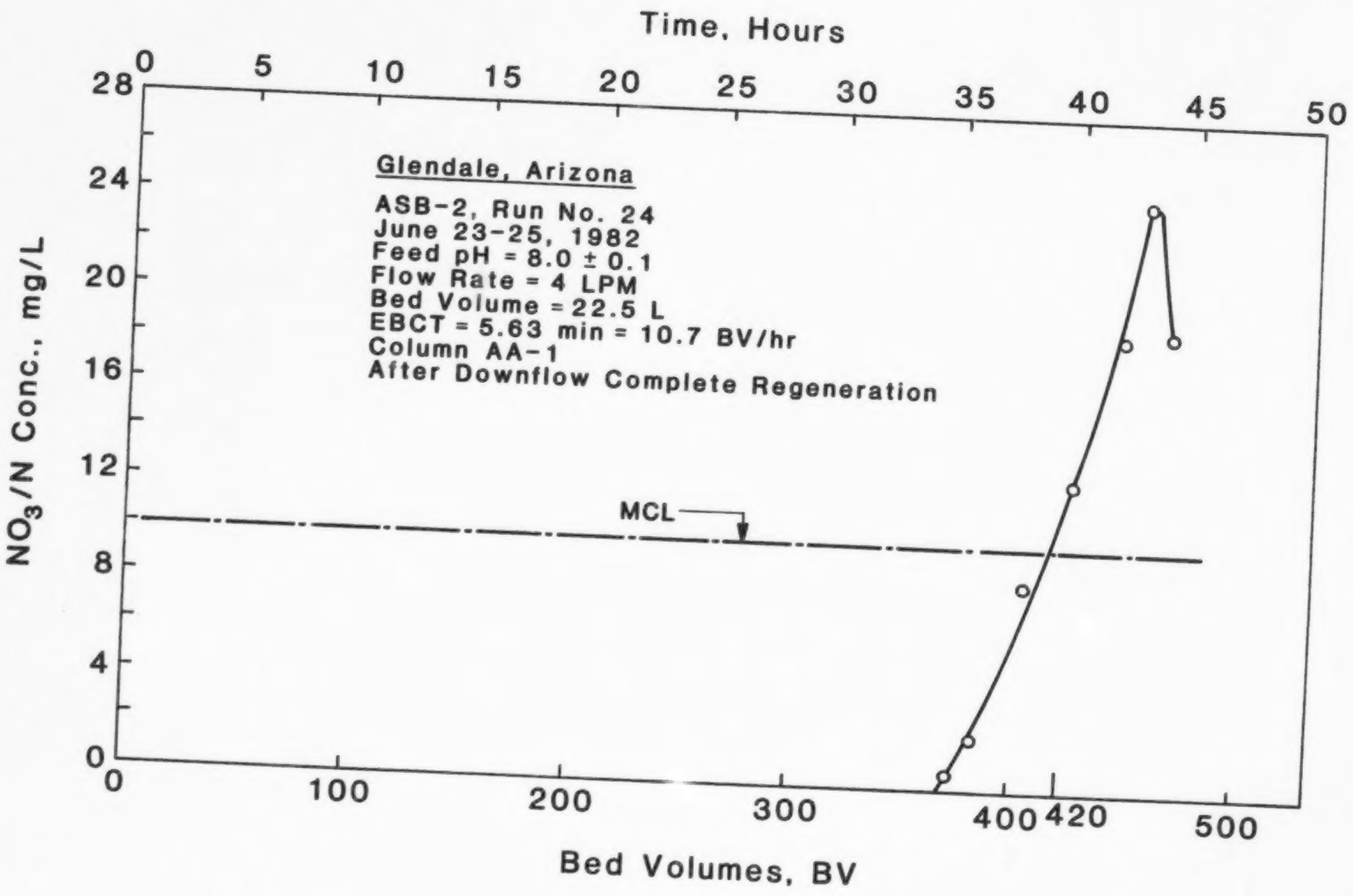


Figure C-24. Exhaustion Run No. 24 following complete regeneration Run 23R.

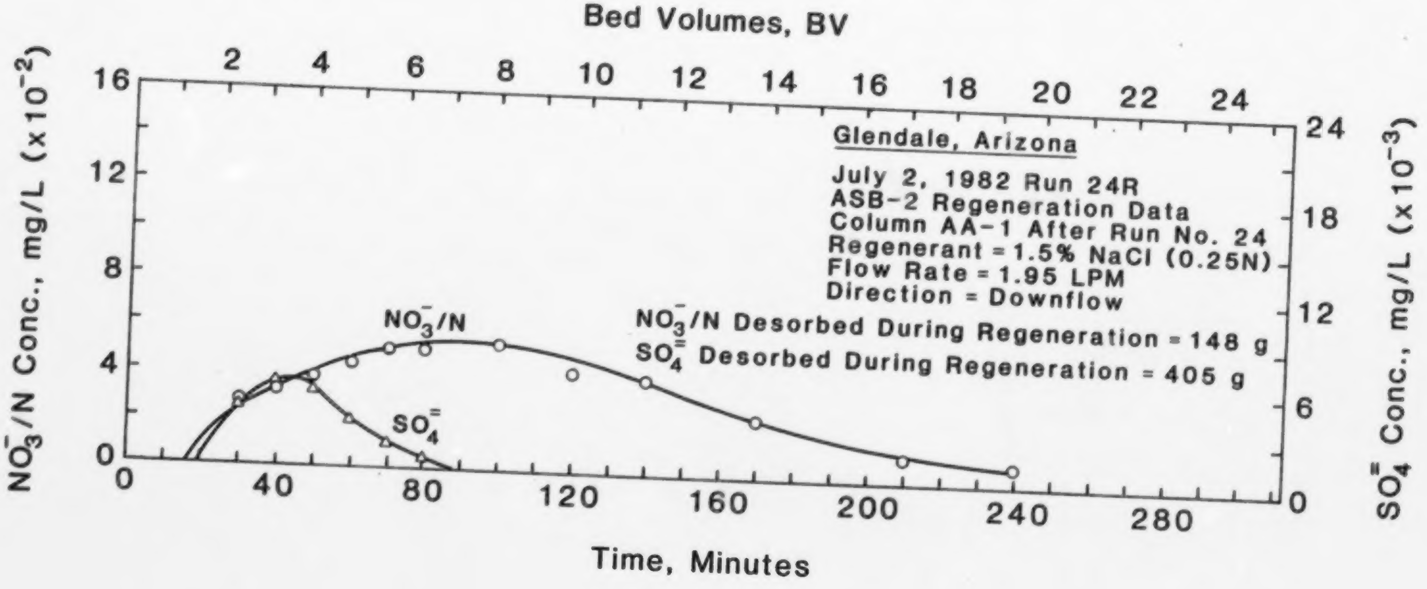


Figure C-24R. Complete regeneration Run No. 24R using 0.25 N NaCl.

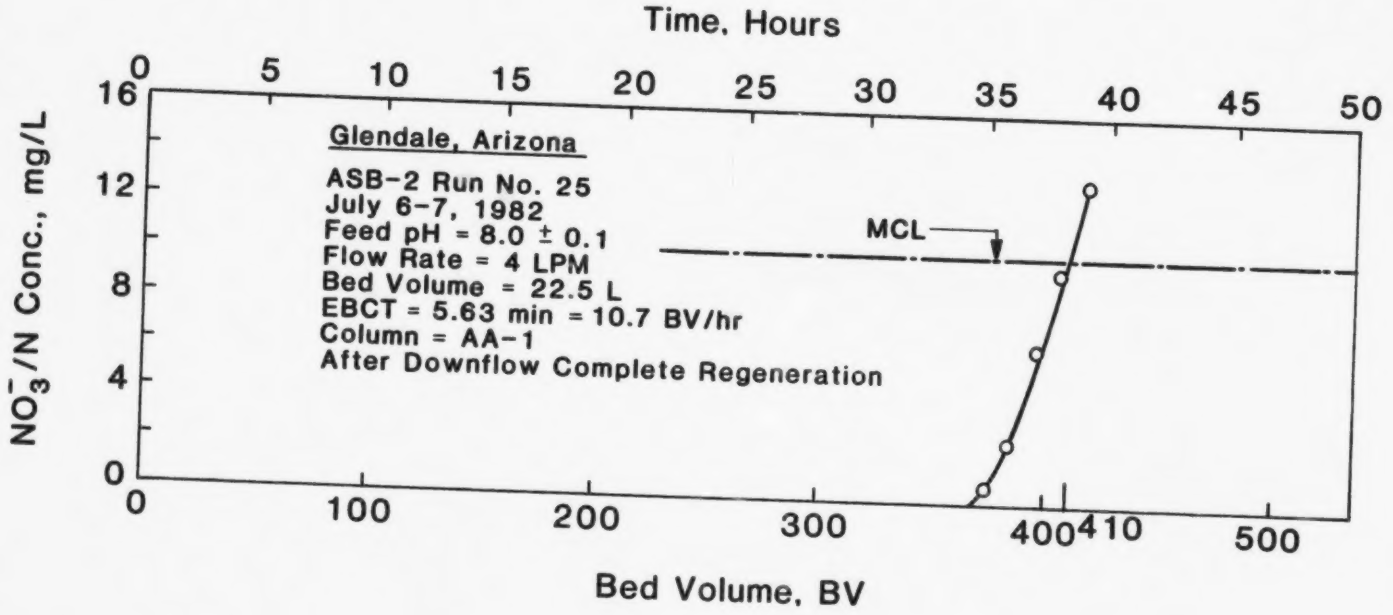


Figure C-25. Exhaustion Run No. 25 following complete regeneration Run 24R.

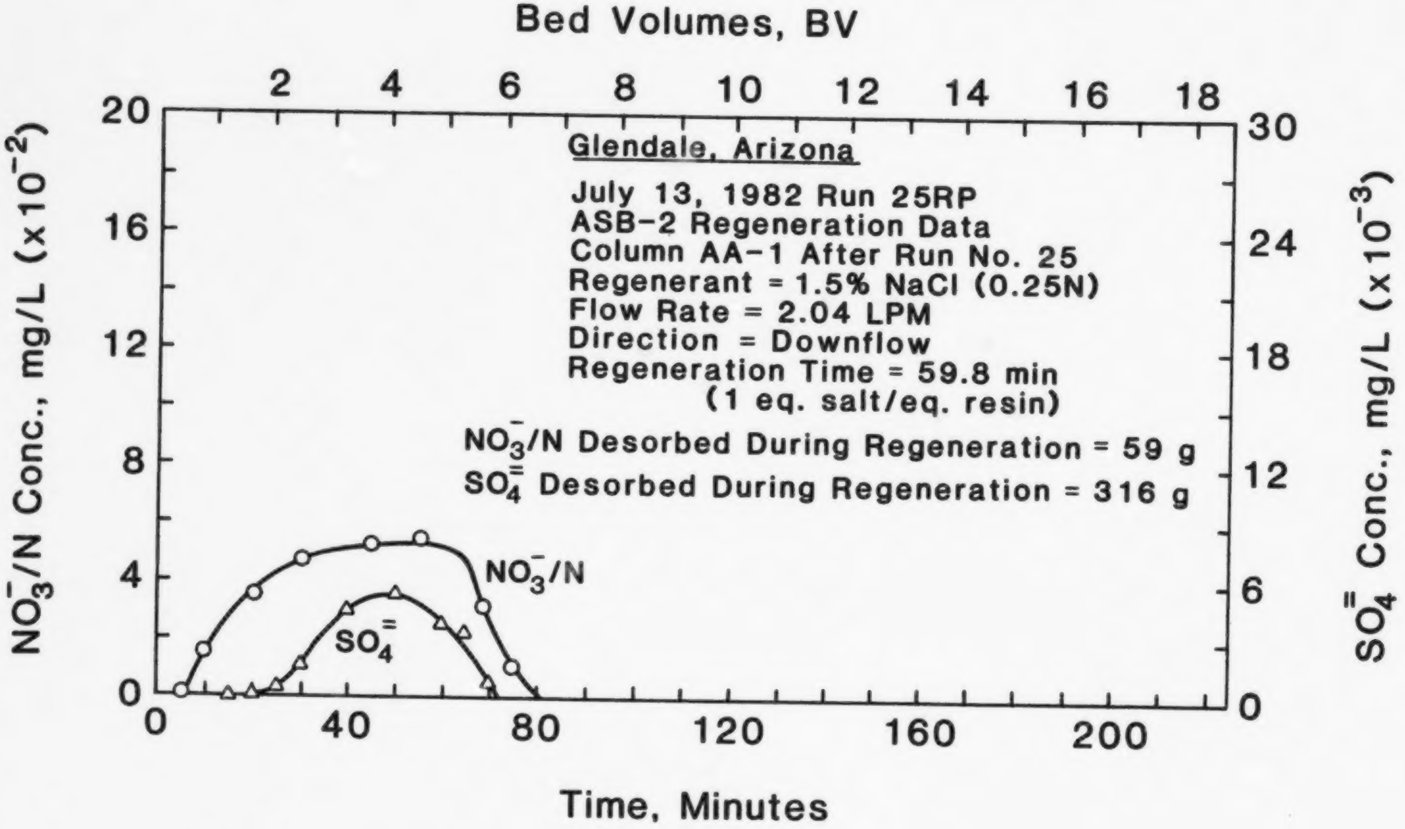


Figure C-25RP. Partial regeneration Run No. 25RP using 0.25 N NaCl at 1.0 equiv. chloride/equiv. resin.

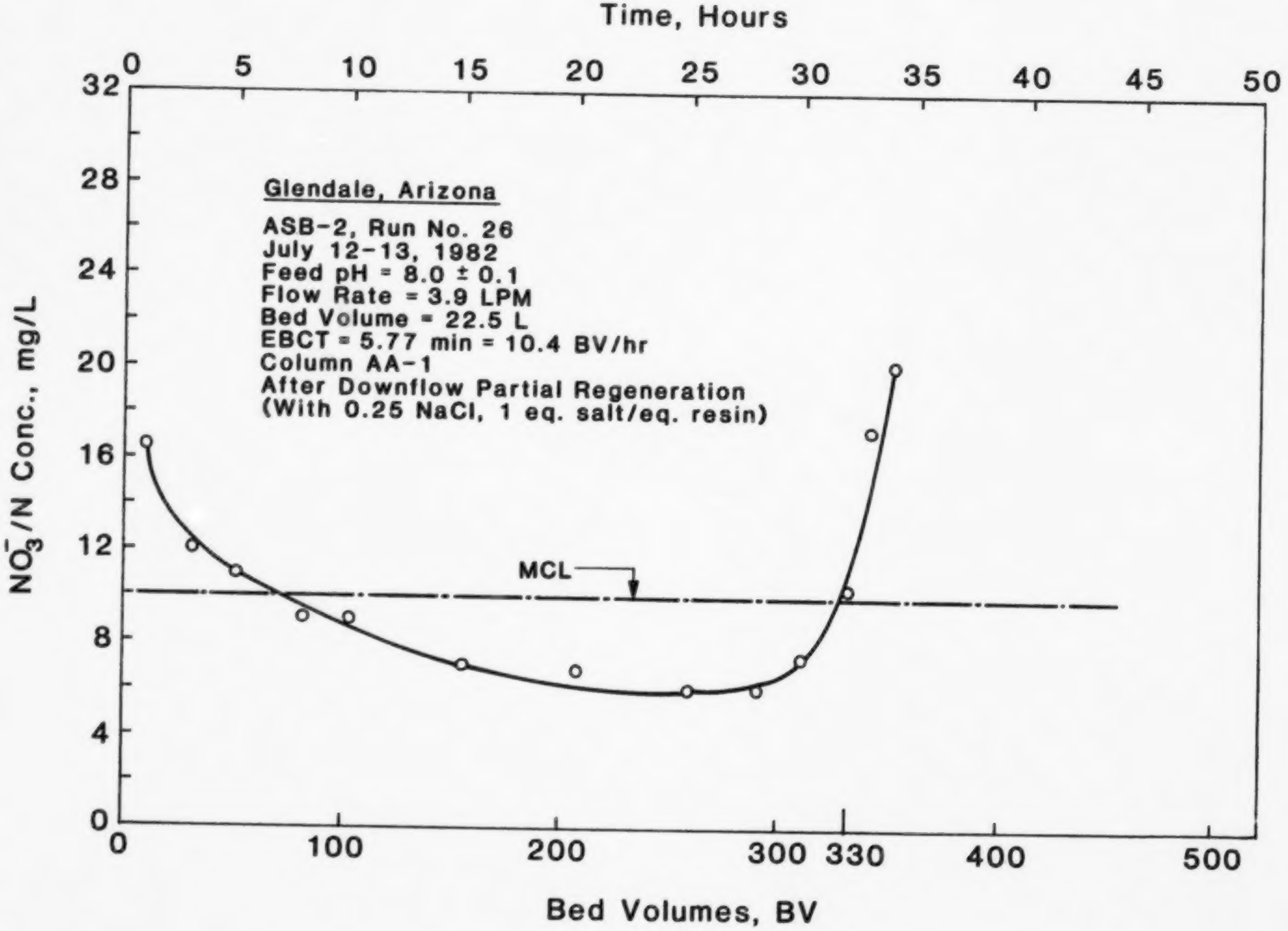


Figure C-26. Exhaustion Run No. 26 following partial regeneration with 1.0 equiv. chloride/equiv. resin.

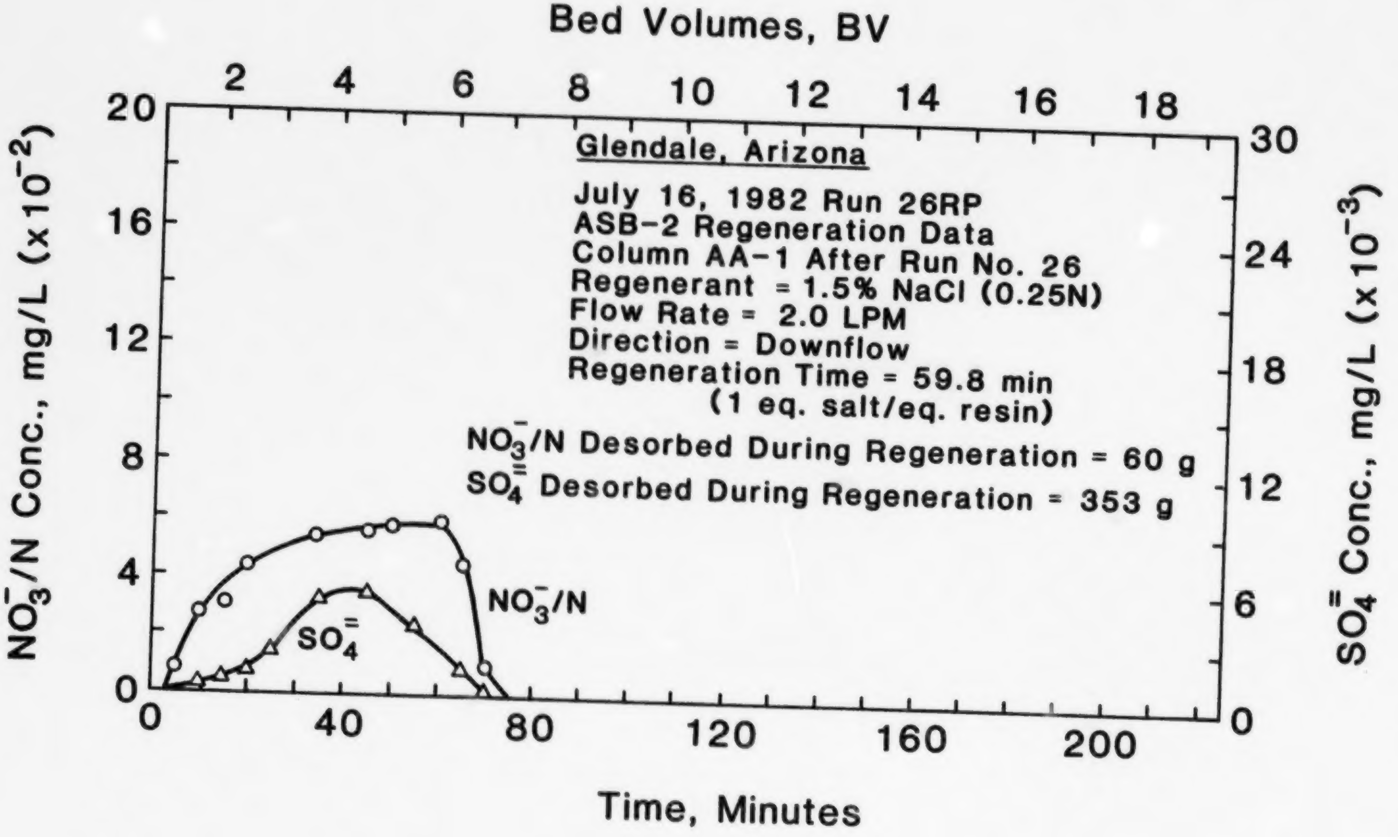


Figure C-26RP. Partial regeneration Run No. 26RP using 0.25 N NaCl at 1.0 equiv. chloride/equiv. resin.

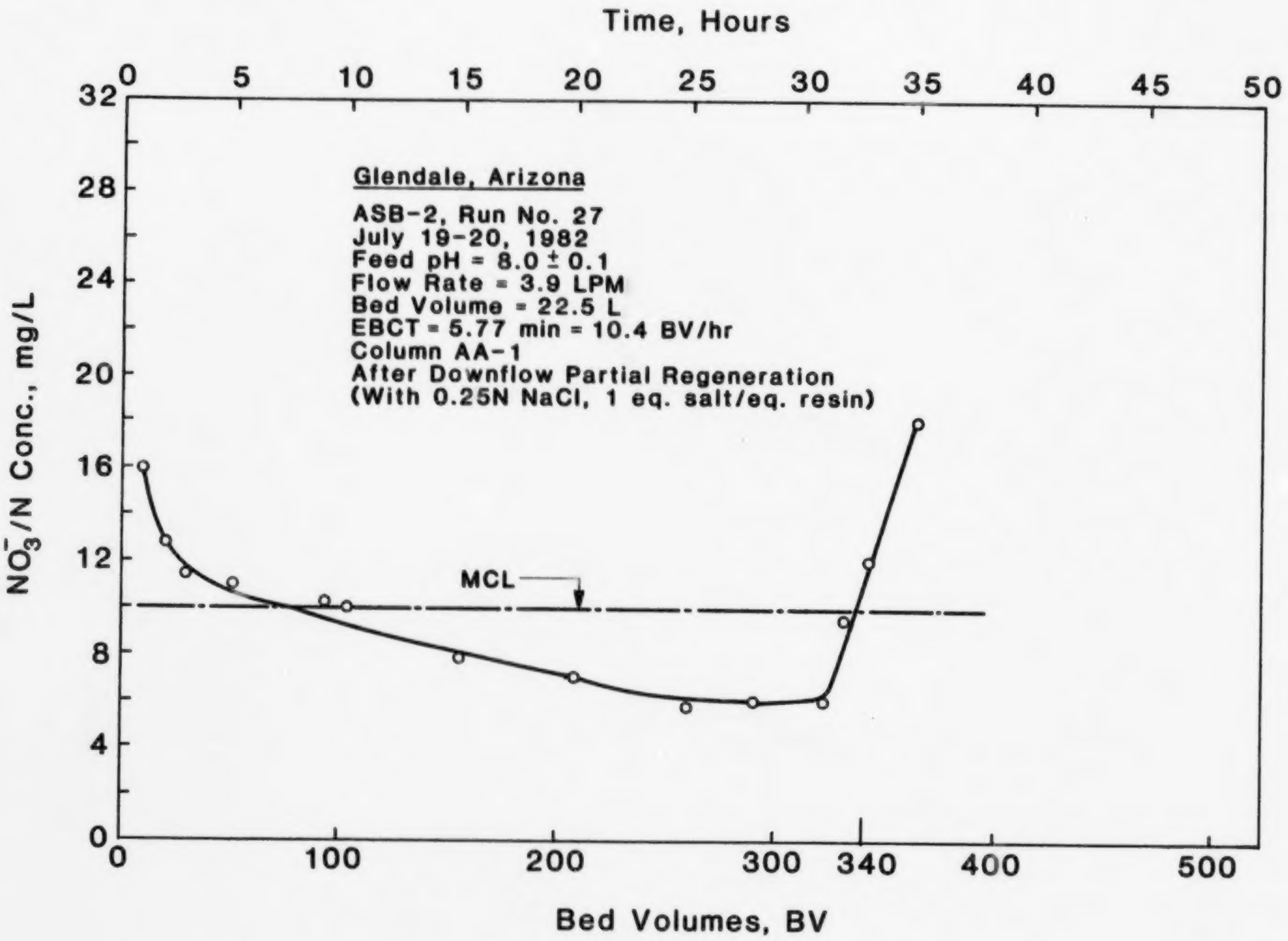


Figure C-27. Exhaustion Run No. 27 following partial regeneration with 1.0 equiv. chloride/equiv. resin.

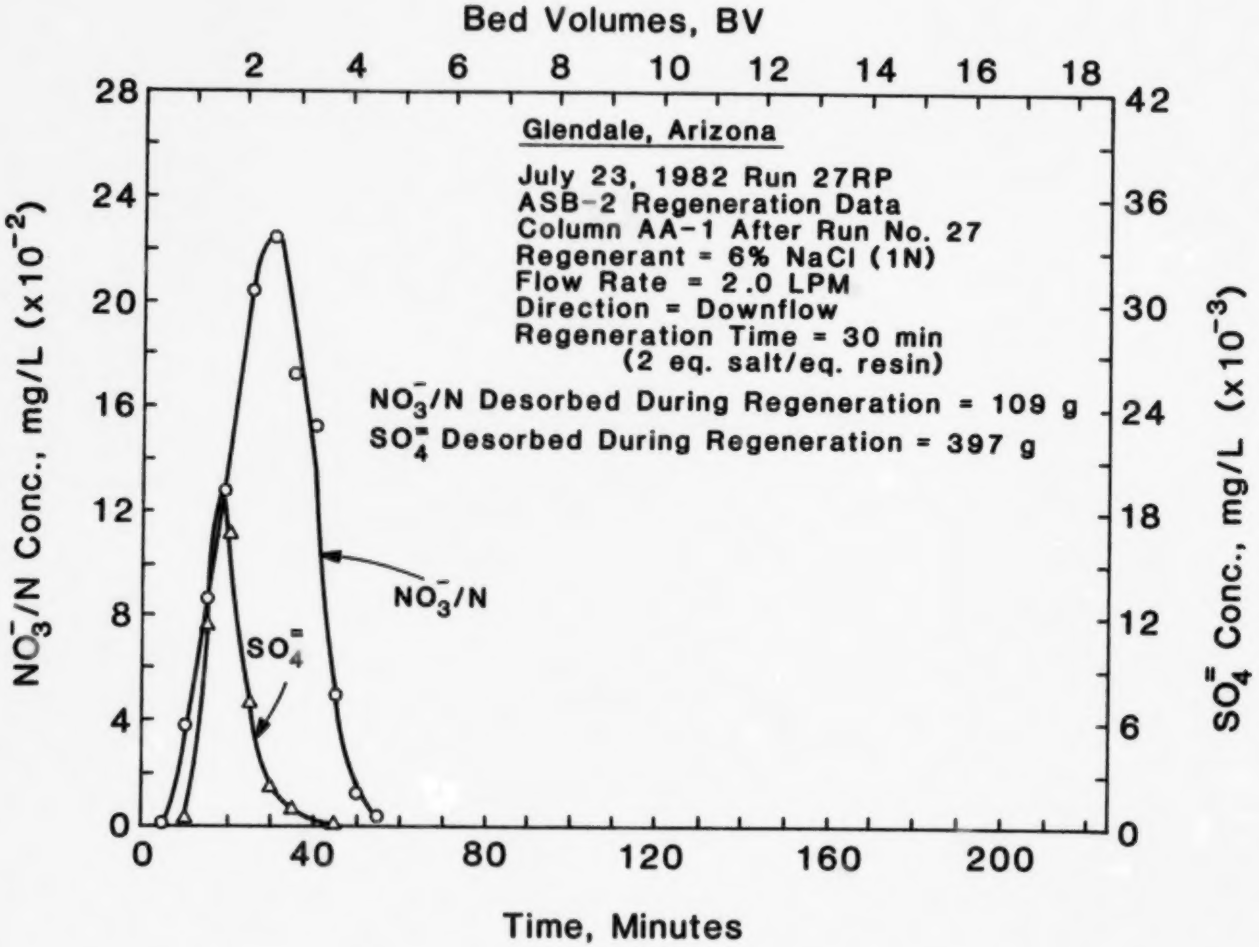


Figure C-27RP. Partial regeneration Run No. 27RP using 1.0 N NaCl at equiv. NaCl/equiv. resin.

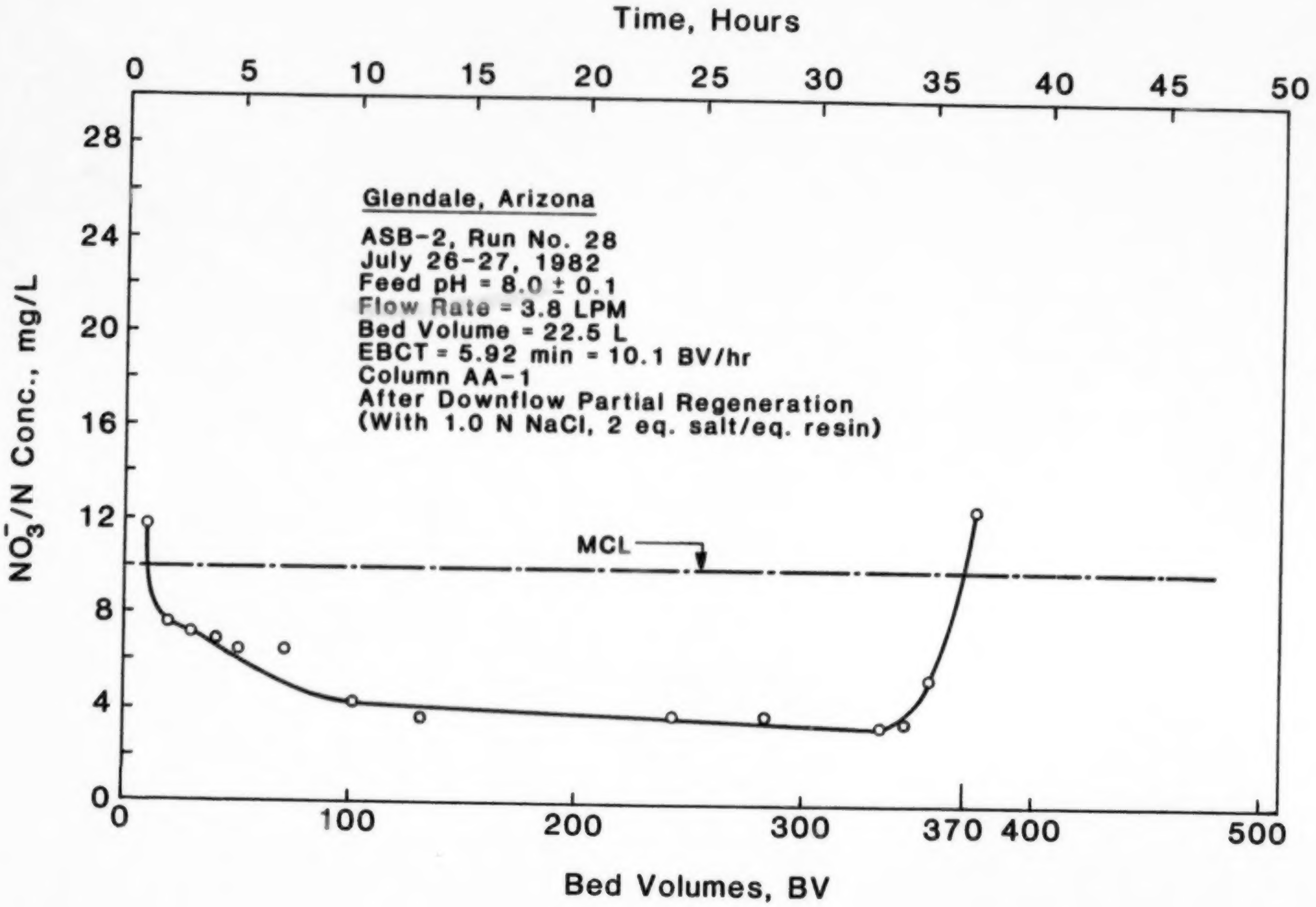


Figure C-28. Exhaustion Run No. 28 following partial regeneration with 2.0 equiv. chloride/ equiv. resin.

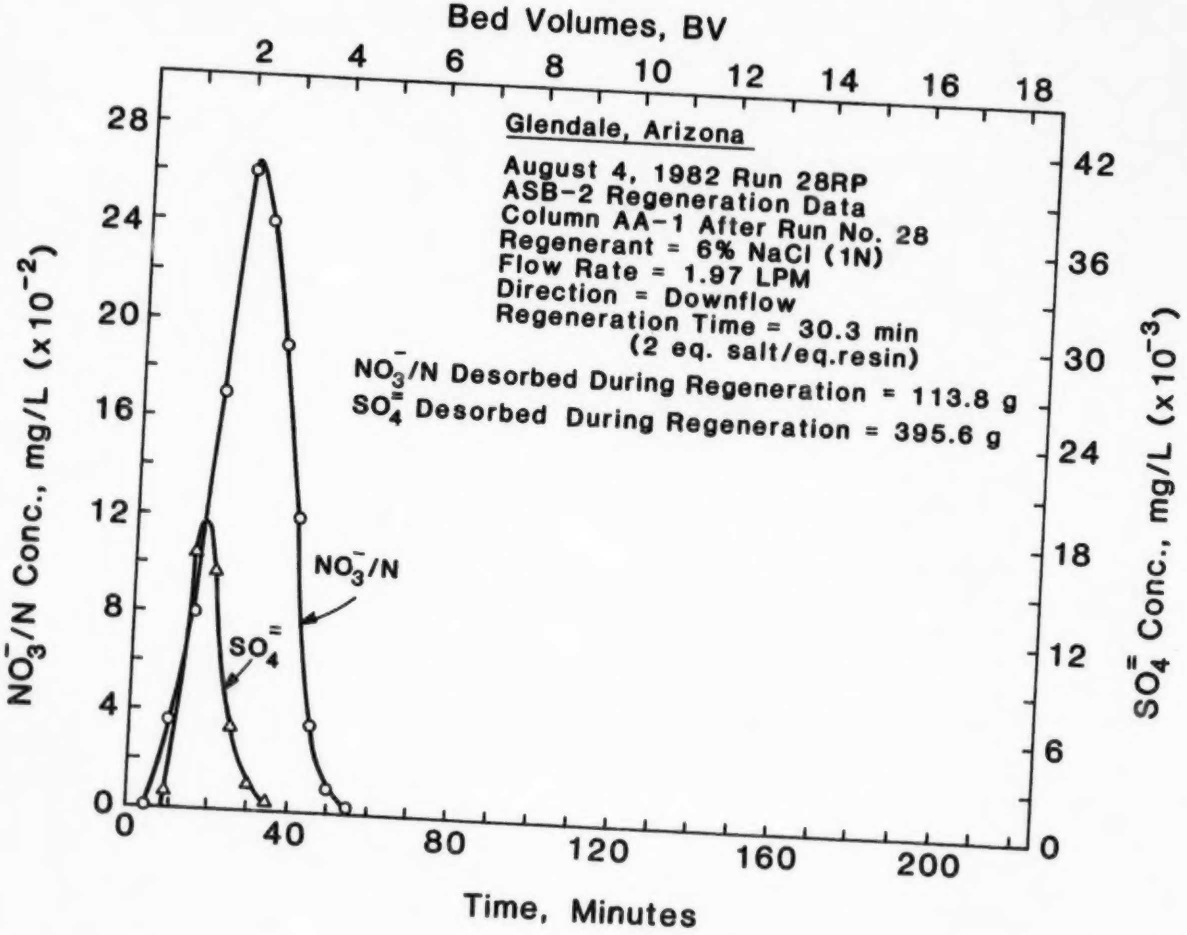


Figure C-28RP. Partial regeneration Run No. 28RP using 1.0 N NaCl at 2.0 equiv. chloride/equiv. resin.

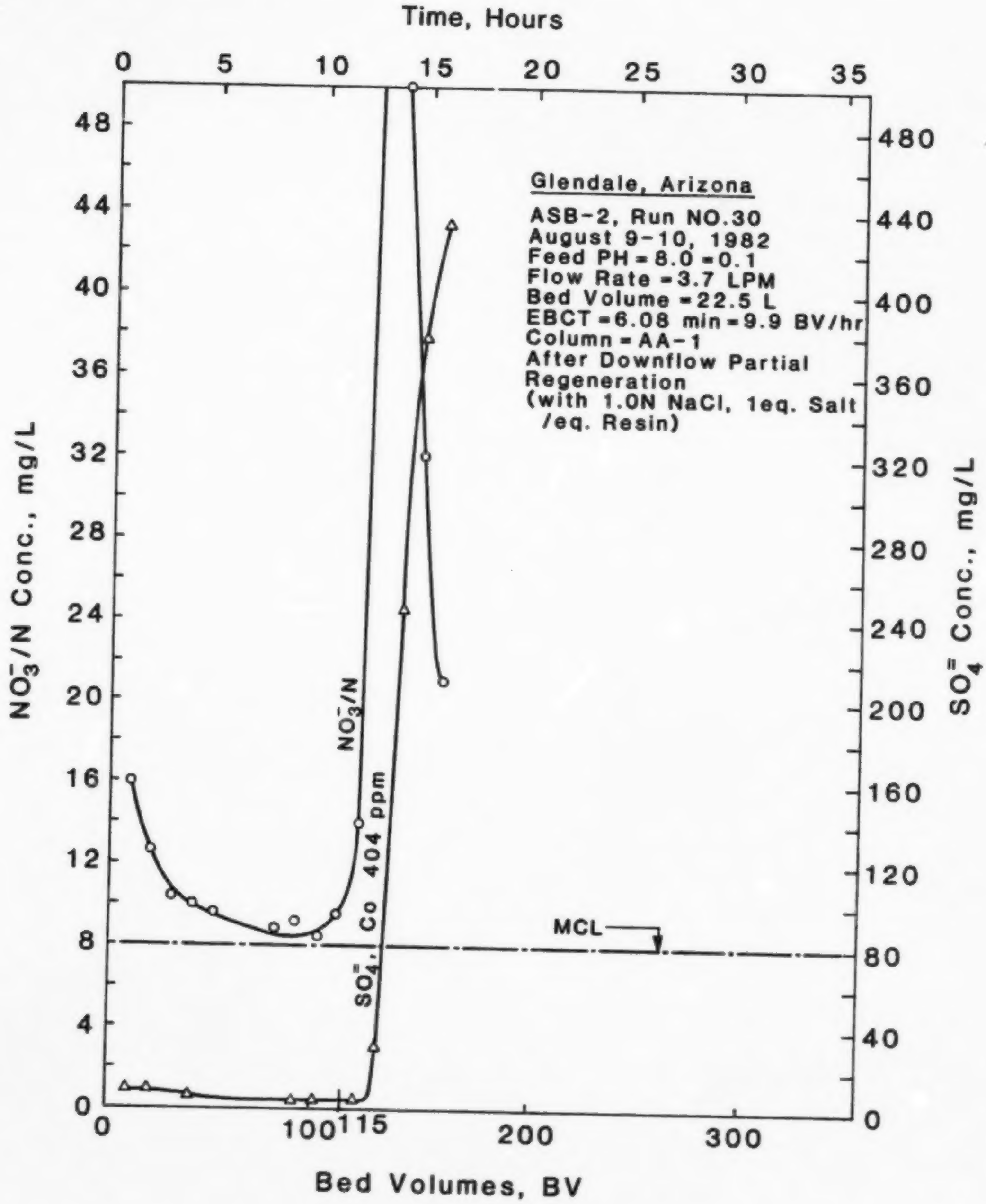


Figure C-30. Exhaustion Run No. 30 with high sulfate, 404 mg/L, feed following partial regeneration with 1.0 equiv. chloride/equiv. resin. Nitrate mostly eluted by sulfate.

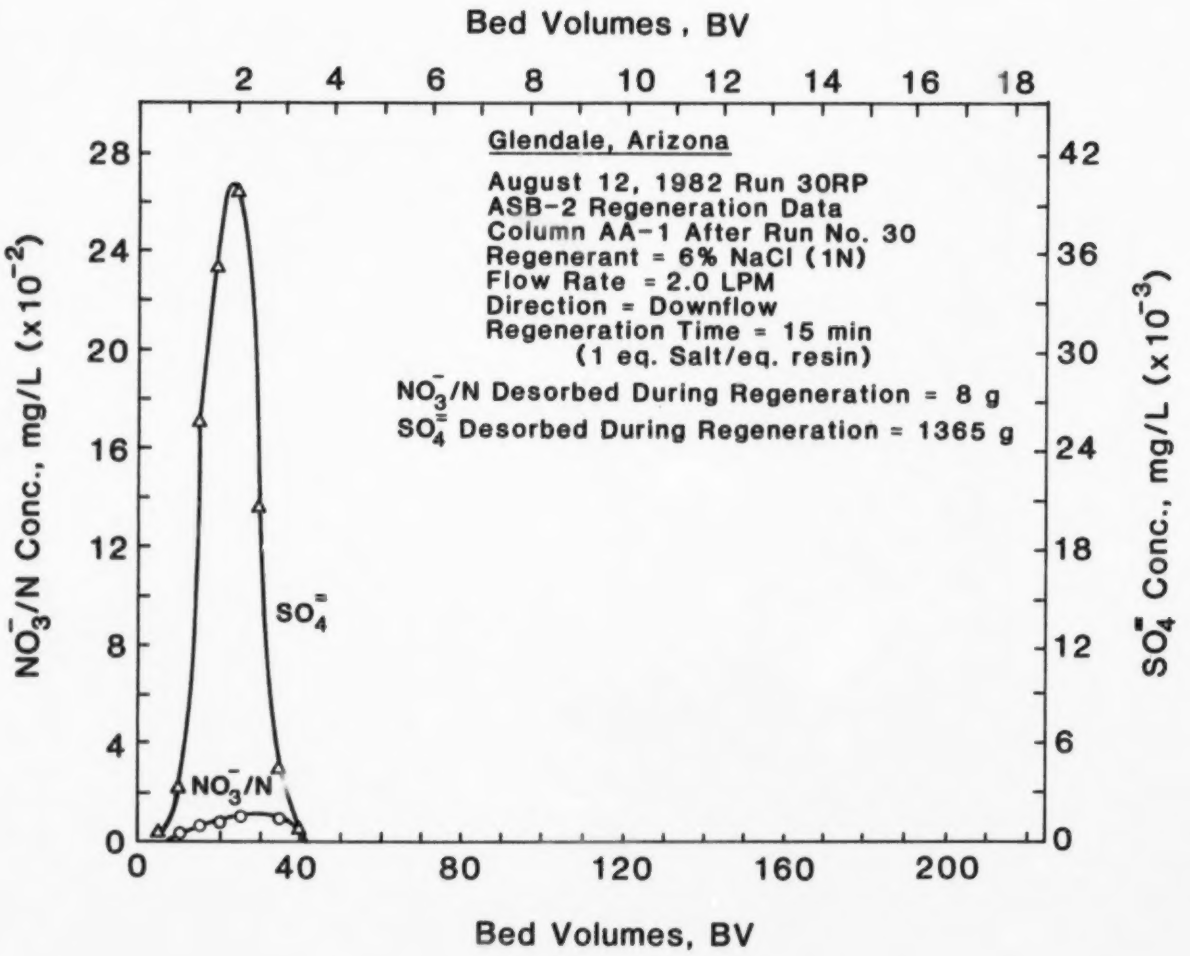


Figure C-30RP. Partial regeneration Run No. 30RP with 1.0 N NaCl at 1.0 equiv. Cl^-/equiv. resin following high-sulfate exhaustion run. Low nitrate elution due to previous elution by sulfate.

APPENDIX D

EXPERIMENTAL PILOT PLANT FACILITIES

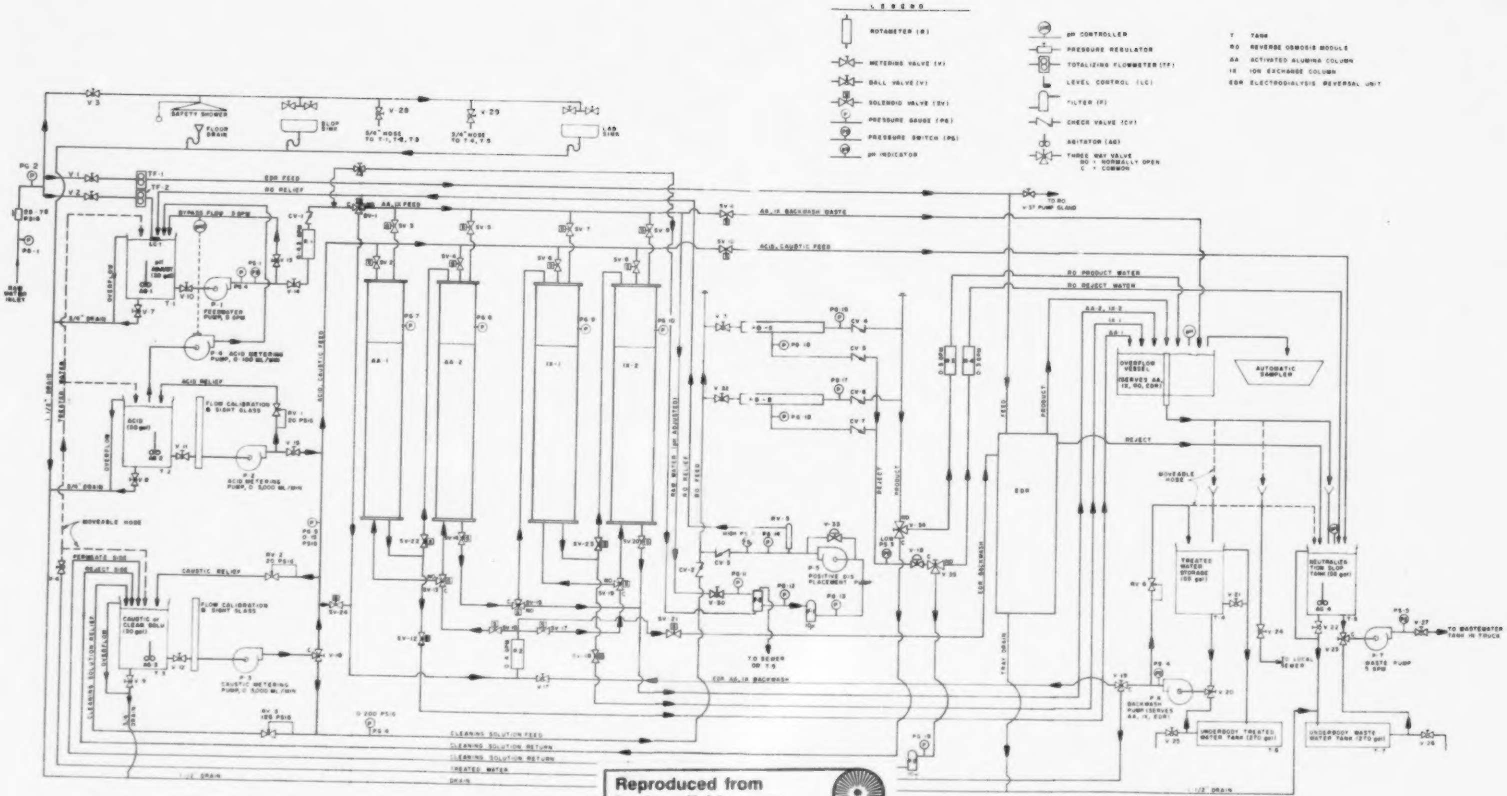
This section of the report gives a detailed description of the pilot plant facilities. Process and instrumentation diagrams for the three pilot plant processes--reverse osmosis, electrodialysis, and ion exchange--are presented along with specifications and operating procedures. An overall process and instrumentation diagram for the entire pilot plant is given in Figure D1.

REVERSE OSMOSIS SYSTEM (Figure D2; Tables D1-D3)

The RO system features two single-pass hollow-fiber modules--one with cellulose triacetate membranes (Dowex, RO-4K) and the other with aramid membranes (DuPont B9). Only one single-pass module was operated during each test which lasted at least 100 hours at 50-75% conversion to determine the rejections of the various ions in the feed. Prior to actual system operation, the optimum pH, pretreatment requirements and estimated % rejections were determined using a computer program (by Dow or DuPont) which made use of the complete chemical analysis of the raw water including its temperature. An example computer prediction for operation of the Dowex 4K Module on the Glendale, Arizona well water is presented in Table D1. Table D2 summarizes the reverse osmosis system design specifications. Figure D2 is a process and instrumentation diagram for the reverse osmosis system.

Acid (H_2SO_4) addition for the prevention of brine-side $CaCO_3$ precipitation was required in both modules according to the computer calculations. pH adjustment was made by H_2SO_4 addition from tank T-2. There was no Cl_2 in the feed water so dechlorination by Na_2SO_3 or granular activated carbon was not required. Sodium hexametaphosphate (SHMP) was pumped from tank T-3 into the raw water tank T-1 for additional scale control.

The pH-adjusted water containing the required additives and the pretreated feedwater was forced through the deep-bed, AG-media filter F-3 and the 10-um cartridge filter F-1 using a combination of the discharge pressure of the centrifugal feedwater pump P-1 and the suction from the 9-stage, Moyno, RO feedwater pump P-5. Control of the feed pressure, flow rate, and % recovery from Module RO-1 or RO-2 were achieved by adjusting the RO pump bypass valve V-33 and the brine discharge V-18. Brine was discharged into the waste tank T-5 while the product water flowed through the overflow vessel from which it was


LEGEND
ROTAMETER (R)
METERING VALVE (V)
BALL VALVE (V)
SOLENOID VALVE (SV)
PRESSURE GAUGE (PG)
PRESSURE SWITCH (PS)
pH INDICATOR
pH CONTROLLER
PRESSURE REGULATOR
TOTALIZING FLOWMETER (TF)
LEVEL CONTROL (LC)
FILTER (F)
CHECK VALVE (CV)
AGITATOR (AG)
THREE WAY VALVE
NO = NORMALLY OPEN
C = COMMON
T TANK
RO REVERSE OSMOSIS MODULE
AA ACTIVATED ALUMINA COLUMN
IX ION EXCHANGE COLUMN
EDR ELECTRODIALYSIS REVERSAL UNIT
RAW WATER INLET
SAFETY SHOWER
FLOOR DRAIN
SLOP SINK
LAB SINK
V-28
V-29
3/4" HOSE TO T-1, T-6, T-3
3/4" HOSE TO T-4, T-5
EDR FEED
RO RELIEF
BYPASS FLOW 3 GPM
AA, IX FEED
AA, IX BACKWASH WASTE
ACID, CAUSTIC FEED
TO RO V-37 PUMP GLAND
P-1 FEEDWATER PUMP, 5 GPM
P-2 ACID METERING PUMP, 0-100 ML/MIN
ACID (30 gal)
ACID RELIEF
FLOW CALIBRATION & SIGHT GLASS
ACID METERING PUMP, 0-5,000 ML/MIN
MOVEABLE HOSE
PERMEATE SIDE
REJECT SIDE
CAUSTIC RELIEF
CAUSTIC or CLEAN SOLN (30 gal)
P-3 CAUSTIC METERING PUMP, 0-5000 ML/MIN
CLEANING SOLUTION FEED
CLEANING SOLUTION RETURN
TREATED WATER
DRAIN
1 1/2" DRAIN
AA-1
AA-2
IX-1
IX-2
RAW WATER (pH ADJUSTED)
RO FEED
RO RELIEF
REJECT
PRODUCT
P-5 POSITIVE DISPLACEMENT PUMP
TO SEWER OR T-5
EDR AA, IX BACKWASH
FEED
EDR
TRAY DRAIN
EDR BACKWASH
RO PRODUCT WATER
RO REJECT WATER
OVERFLOW VESSEL (SERVES AA, IX, RO, EDR)
AUTOMATIC SAMPLER
TREATED WATER STORAGE (55 gal)
NEUTRALIZATION SLOP TANK (55 gal)
P-6 BACKWASH PUMP (SERVES AA, IX, EDR)
P-7 WASTE PUMP 5 GPM
TO LOCAL SEWER
TO WASTEWATER TANK IN TRUCK
UNDERBODY TREATED WATER TANK (270 gal)
UNDERBODY WASTE WATER TANK (270 gal)

Reproduced from best available copy.

Figure D1 Process and instrumentation schematic for the four processes (AA1, IX, RO, EDR) in the UH/EPA Mobile Water Treatment Pilot Plant.

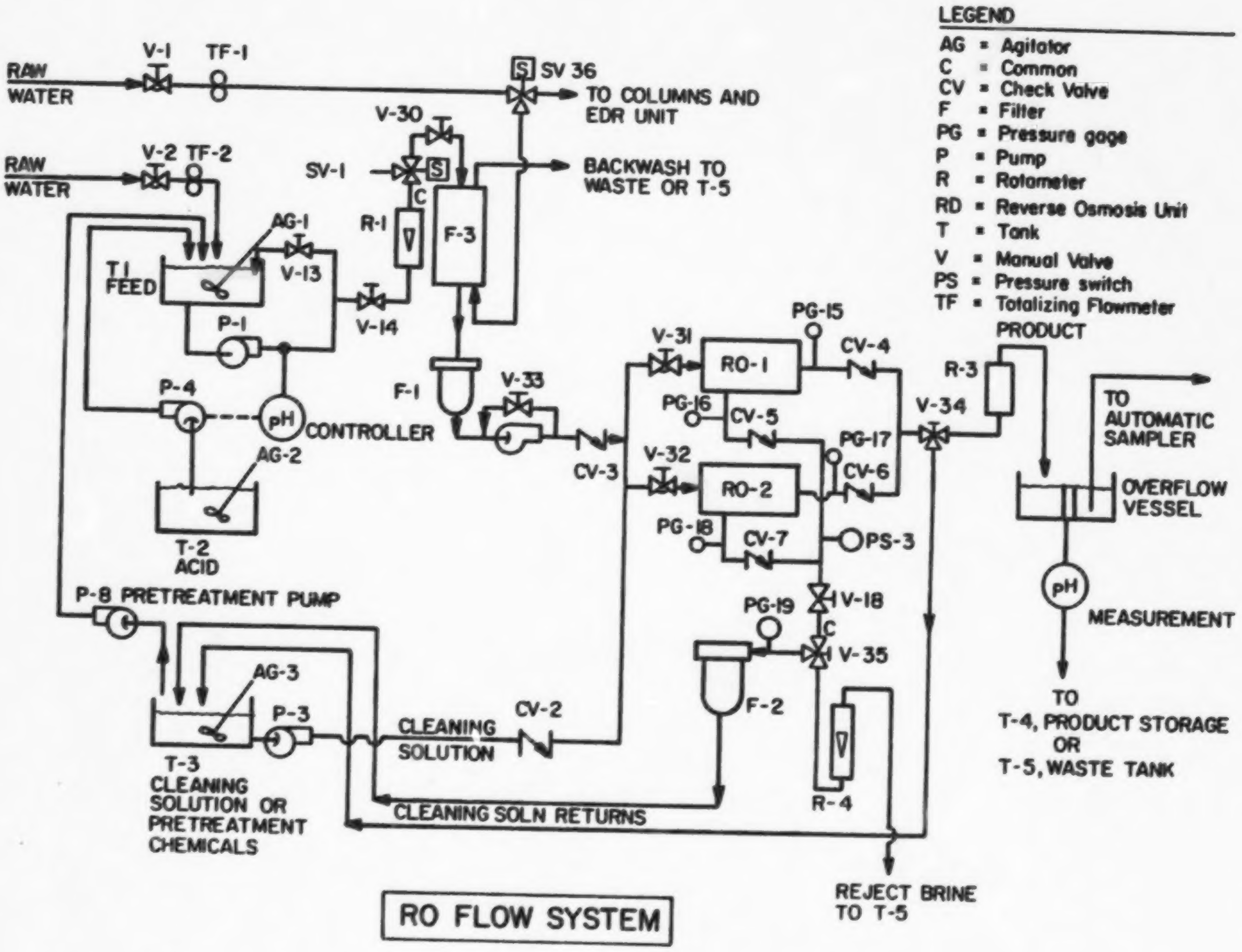

LEGEND
AG = Agitator
C = Common
CV = Check Valve
F = Filter
PG = Pressure gage
P = Pump
R = Rotameter
RD = Reverse Osmosis Unit
T = Tank
V = Manual Valve
PS = Pressure switch
TF = Totalizing Flowmeter
RAW WATER
V-1
TF-1
RAW WATER
V-2
TF-2
SV 36
TO COLUMNS AND EDR UNIT
V-30
SV-1
C
BACKWASH TO WASTE OR T-5
AG-1
V-13
T1 FEED
R-1
F-3
P-1
V-14
P-4
pH
CONTROLLER
AG-2
T-2 ACID
F-1
V-33
CV-3
V-31
RO-1
PG-15
CV-4
PG-16
CV-5
PG-17
V-32
RO-2
CV-6
PG-18
CV-7
PS-3
V-18
PG-19
V-35
F-2
R-4
V-34
R-3
PRODUCT
TO AUTOMATIC SAMPLER
OVERFLOW VESSEL
pH
MEASUREMENT
TO T-4, PRODUCT STORAGE OR T-5, WASTE TANK
P-8 PRETREATMENT PUMP
AG-3
P-3
T-3 CLEANING SOLUTION OR PRETREATMENT CHEMICALS
CLEANING SOLUTION
CV-2
CLEANING SOLN RETURNS
REJECT BRINE TO T-5
RO FLOW SYSTEM

Figure D-2. Process and instrumentation diagram for the reverse osmosis (RO) system.

TABLE D1
DOWEX* R.O. PERMEATOR SYSTEM DESIGN
UNIVERSITY OF HOUSTON

		Water Analysis			
Ion	ppm Ion in Raw Feed	ppm Ion in Treated Feed	ppm $CaCO_3$ in Treated Feed	ppm Ion in Permeate	ppm Ion in Concentrate
Ca^{++}	46.00	46.00	115.00	1.29	90.71
Na^{++}	76.00	76.00	165.68	6.17	145.83
Mg^{++}	28.00	28.00	115.08	0.63	55.37
Fe^{++}	0.10	0.10	0.18	0.00	0.20
Mn^{++}	0.00	0.00	0.00	0.00	0.00
K^{+}	0.00	0.00	0.00	0.00	0.00
$Total^{+}$	150.10	150.10	395.94	8.10	292.10
Cl^{-}	131.00	131.00	184.51	3.30	258.70
F^{-}	0.50	0.50	1.32	0.02	0.98
SO_4^{2-}	43.00	76.50	79.69	1.47	151.54
NO_3^{-}	97.40	97.40	78.89	12.30	182.50
S_iO_2	23.00	23.00	38.41	1.60	44.40
PO_4^{3-}	0.00	0.00	0.00	0.00	0.00
HCO_3^{-}	124.00	81.49	66.80	3.73	159.25
CO_3^{2-}	0.00	0.00	0.00	0.00	0.00
$Total^{-}$	418.90	386.89	411.20	20.81	752.98
Grand Total	569.00	559.99	441.98	30.50	1089.48
pH	8.00	6.60		5.75	6.81
CO_2		33.42		25.07	
Langelier Index					-0.26

TABLE D1 (continued)

Optimized Design Configuration and Ratings

Stage No.	Permeators per Stage	Avg. Unit Prod(GPD)	Total Prod Flow(GPD)	Total Brine Flow(GPD)	Pct. Pec.	Pct. Pej.	Delta (Psi)
1	1	5846.	5846.	5846.	50.00		5.
Overall	1	5846.	5846.	5846.	50.00	94.55	

Notes: A 1 stage system with 1 permeators (std. test performance of 4000 gpd. 90.0% rejection) operating at 400 psi and interstage pressure loss of 0 psi. Overall system recovery is 50% design feed temperature is 35.0 degree C.

Assumptions: Sterile feedwater, injection of appropriate scale inhibitor and acidification for carbonate scale ctpl:
0.29 lbs H_2SO_4(100 pct)/kgal feed.

Maximum recovery to avoid saturation with:

Gypsum	100%	$CaSO_4$ Anhydrite	100%
Barium sulfate	100%	Strontium sulfate	100%

This estimate of an appropriate design configuration and expected performance of DOWEX* P.O. permeators is based upon the particular feedwater analysis submitted to the DOW Chemical Co. The design and expected performance are presented in good faith. But no warranty is expressed or implied. Although these criteria should assure proper performance of the DOWEX* R.O. permeators. The ultimate success of any R.O. facility depends upon an adequately engineered system that is properly operated and maintained.

*Trademark of the DOW Chemical Company.

TABLE D2
REVERSE OSMOSIS SYSTEM SPECIFICATIONS

Number of Modules: Two in parallel

Mode of Operation: Module 1 or Module 2

Module 1: duPont Model No. 0420-21
- Membrane Type: B-9 Aramid
- Membrane Configuration: Hollow Fiber
- Shell Dimensions: 13.3 cm OD x 63.5 cm long (5.25 in OD x 25 in long)
- Product Water Capacity: 7.95 m^3/day (2,100 gpd at 1500 ppm TDS)
- Operating Pressure: 0-2760 kPa (0-400 psig)
- Operating Temperature: 0-35°C (32-95°F)
- pH Range, Continuous: 4-11
- Minimum Brine Rate: 4.2 L/min (1.11 gpm)
- Chlorine Tolerance: Cl_2 must be removed
- Silt Density Index, SDI: ≤ 3.0

Module 2: Dow Model Dowex 4K
- Membrane Type: Cellulose Triacetate
- Membrane Configuration: Hollow Fiber
- Shell Dimensions: 15.88 cm OD x 122 cm long (6.25 in OD x 48 in long)
- Product Water Capacity: 15.14 m^3/day (4,000 gpd at 1500 ppm TDS)
- Operating Pressure: 0-2760 kPa (0-400 psig)
- Operating Temperature: 0-30°C (32-86°F)
- pH Range, Continuous: 4.0 - 7.5
- Minimum Brine Rate: 1.9 L/min (0.5 gpm)
- Chlorine Tolerance: ≤ 1.0 mg/L
- Silt Density Index, SDI: ≤ 4.0

RO Pump: Moyno 9P3, 316 ss Rotor
- Maximum Pump Pressure; 5520 kPa (800 psig)
- Pump Operating Pressure; 2760 kPa (400 psig)
- Pump Motor: 3 hp, 220 v, Single Phase
- High Pressure Cutoff: 3105 kPa (450 psig)
- High Pressure Relief: 3105 kPa (450 psig)
- Low Pressure Cutoff: 2070 kPa (300 psig)

RO Pretreatment Filters: Two Provided--One Deep Bed, One 10-um Cartridge
- Deep Bed Filter: 35.6 cm OD x 165 cm height (14 in OD x 65 in height)
- Filter Media: 76.2 cm AG over 10 cm flint gravel (30 in AG over 4 in flint gravel)
- Filtration Rate: 117-293 m/day (2-5 gal/min ft^2)

sampled every four hours by the automatic sampler.

Testing the RO units in the Arizona summer caused some temperature problems. During the hottest summer days, the outside air temperature reached 120°F (49°C) and the feedwater entering the pilot plant from the water tower reached 113°F (45°C) due to solar and convective heating of the inlet piping and tubing. Since the suggested maximum operating temperatures of the Dow and DuPont modules are 30°C and 35°C respectively, feedwater cooling had to be provided. This was accomplished by making tank T-4 into an ice bath which consumed approximately 300 lbs (136 kg) of block ice per day. Ice water from T-4 was pumped by P-6 through a copper cooling coil immersed in the feedwater tank T-1. The cooling water flow rate was adjusted by value V-4 to keep the RO feedwater temperature below 35°C (95°F). Using this procedure, the cooled feedwater temperature was measured at 31 ± 4°C. This method was so costly and cumbersome that testing the Dowex 4K RO module with its 30°C maximum operating temperature was deferred until cooler weather.

Note that these unusually high water temperatures were due to the long storage time and abnormally low flow rate (2-5 gpm) from the 150,000 gallon elevated storage tank which was being filled only for our pilot plant tests. The actual groundwater temperature pumped from the No. 1 well did not exceed 25°C.

When tests were completed on each of the RO modules, they were filled with a 1% by weight aqueous solution of formaldehyde to prevent bacterial growth. The pilot plant is provided with means for cleaning the RO modules with acid, chelating agents and enzymes, but this was found to be unnecessary following the Glendale experiments.

The operating variables to be studied during contaminant and desalting with the RO unit are listed in Table D3.

ELECTRODIALYSIS SYSTEM (Figures D3-D4, Tables D4-D5)

The reversible electrodialysis unit was purchased essentially as a complete unit (Aquamite I) from the manufacturer (Ionics, Inc.). That was done because the package unit was the only electrodialysis device commercially available in pilot scale. Figure D3 illustrates how the package unit was incorporated into the overall process flow system. It is not a complete flow schematic because within the EDR unit there are many additional components. The internal flow scheme of the Aquamite I is shown in Figure D4 and described in Table D4. The operating variables studied are listed in Table D5.

Desalting and contaminant removal at 50-80% recovery were achieved by feeding pressurized raw water, usually without pretreatment or scale control additives, through manual valve V-1 (Figure D4) directly to the EDR unit. Because the unit was set up by the manufacturer with internal brine recycle to achieve 80% recovery, it is usually run in that mode rather than in the no recycle, 50% recovery mode. Product water flowed

TABLE D3
REVERSE OSMOSIS (RO): INDEPENDENT AND DEPENDENT VARIABLES TO BE STUDIED DURING NITRATE REMOVAL TESTS

Membrane material: hollow fiber aramid (duPont), or cellulose triacetate (Dow)

*Method of reducing fouling index of feed: deep bed filtration with "AG" media or "Electromedia"; AG media with and without polymer addition

*Dechlorination methods: Na_2SO_3, granular activated carbon

Feedwater additives to prevent ppt of $CaCO_3$: Polyphosphates

pH of feedwater: adjusted by H_2SO_4 or HCl addition

pH of product water: continuous monitoring

Feedwater pressure: 1379 to 3447 kPa (200-500 psig)

% TDS removal: based on conductivity and gravimetric methods

% water recovery: (Product flow/feed flow) 100; 40-75%

%rejection of contaminants: $[(C_F - C_P)/C_F]100$

% rejection of common ions: Ca^{++}, Mg^{++}, Na^+, Cl^-, HCO_3^-, $SO_4^=$, SiO_2

*Various methods of cleaning membranes: H_2SO_4, HCl, citric acid, TSP; chelants such as VERSENE or EDTA; HClO, BIZ, etc.

Notes: C_F = Concentration of ion in feed
C_P = Concentration of ion in product
* = Variable not studied in Glendale

through the overflow vessel and was collected in the treated water tanks T-1 and T-6 (This pure product water may be recirculated through the entire system from tank T-1 via pump P-1 directly from tank T-6 via pump P-6.) Reject brine was wasted after flowing through wastewater tank T-5.

During operation of the EDR unit, the current direction, brine and product flows were automatically reversed each 15 minutes thereby providing automatic membrane backwash at each reversal. According to the manufacturers, and as verified by our experience to date (June, 1982), this allows for operation with minimum pretreatment, e.g., no pH adjustment, deep bed filtration, or anti-scaling additives were used. Furthermore, Ionics claims that up to 400% supersaturation of $CaSO_4$ may occur on the brine side without serious fouling. However, we did not verify this latter claim in the Glendale tests.

TABLE D3
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Notes: C_F = Concentration of ion in feed
C_P = Concentration of ion in product
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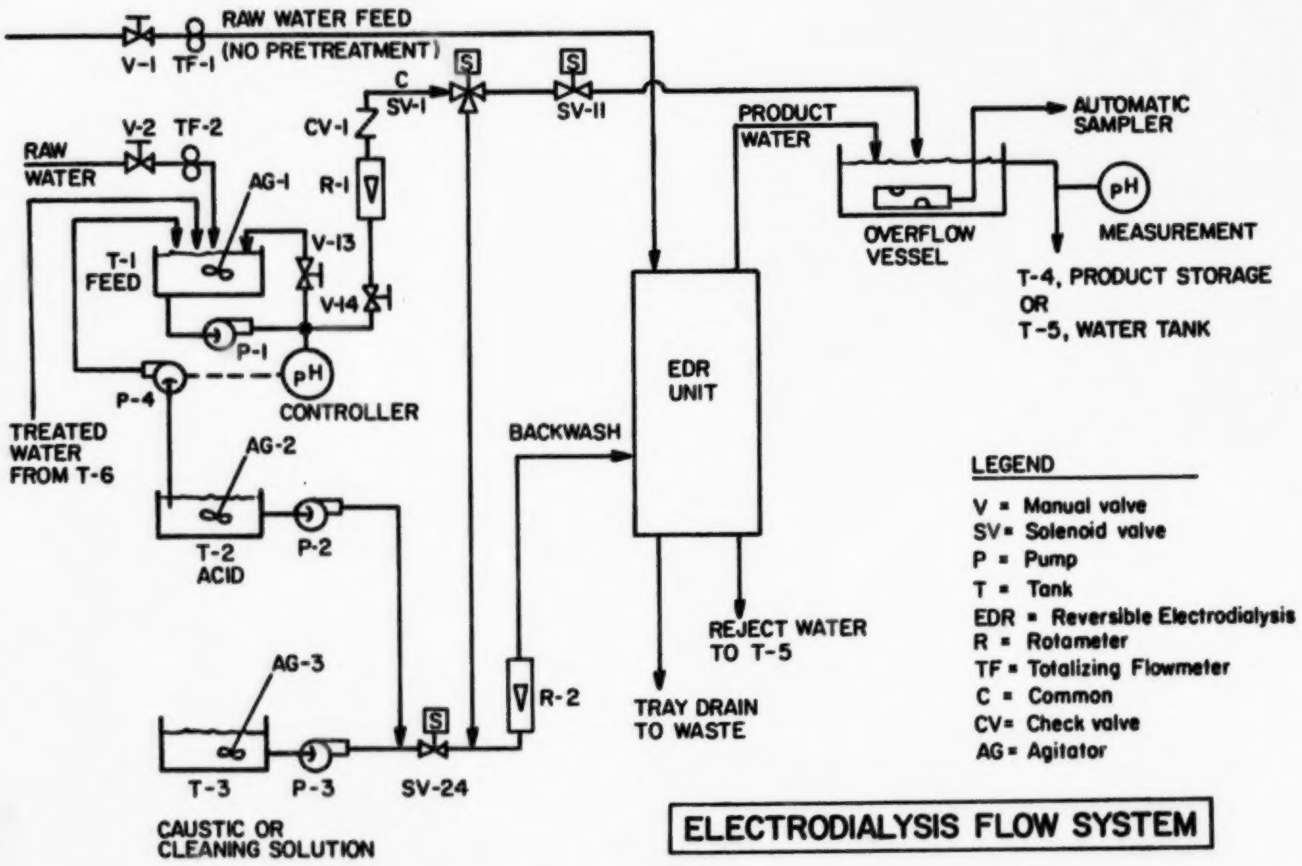
RAW WATER FEED
(NO PRETREATMENT)
V-1
TF-1
C
SV-1
S
SV-11
RAW WATER
V-2
TF-2
AG-1
CV-1
R-1
T-1 FEED
V-13
V-14
P-1
pH
CONTROLLER
P-4
TREATED WATER FROM T-6
AG-2
T-2 ACID
P-2
AG-3
T-3
P-3
SV-24
CAUSTIC OR CLEANING SOLUTION
R-2
BACKWASH
EDR UNIT
PRODUCT WATER
OVERFLOW VESSEL
AUTOMATIC SAMPLER
pH
MEASUREMENT
T-4, PRODUCT STORAGE OR T-5, WATER TANK
REJECT WATER TO T-5
TRAY DRAIN TO WASTE
LEGEND
V = Manual valve
SV = Solenoid valve
P = Pump
T = Tank
EDR = Reversible Electrodialysis
R = Rotameter
TF = Totalizing Flowmeter
C = Common
CV = Check valve
AG = Agitator
ELECTRODIALYSIS FLOW SYSTEM

Figure D-3. Process and instrumentation diagram for the reversible electrodialysis (EDR) system.

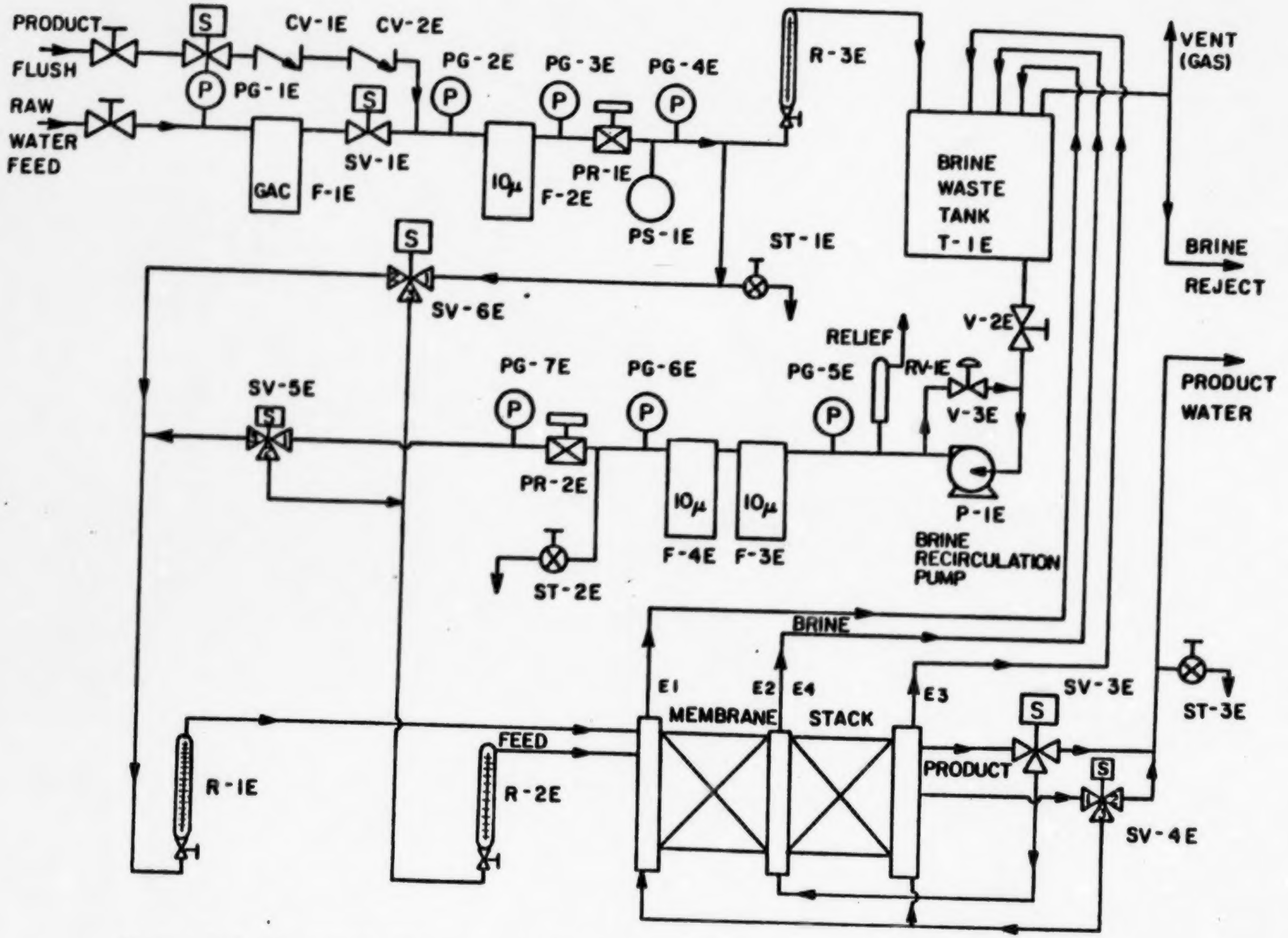
PRODUCT
FLUSH
RAW
WATER
FEED
S
P
PG-1E
CV-1E
CV-2E
GAC
F-1E
S
SV-1E
PG-2E
P
10μ
F-2E
PG-3E
P
PR-1E
PG-4E
P
PS-1E
R-3E
BRINE
WASTE
TANK
T-1E
VENT
(GAS)
BRINE
REJECT
S
SV-6E
ST-1E
RELIEF
RV-1E
V-2E
V-3E
PRODUCT
WATER
SV-5E
S
PG-7E
P
PR-2E
PG-6E
P
10μ
F-4E
10μ
F-3E
PG-5E
P
P-1E
BRINE
RECIRCULATION
PUMP
ST-2E
BRINE
E1
E2
E4
E3
MEMBRANE
STACK
FEED
R-1E
R-2E
PRODUCT
S
SV-3E
S
SV-4E
ST-3E

Figure D-4. Internal flow schematic for the Ionics EDR unit shown in Figure

TABLE D4
REVERSIBLE ELECTRODIALYSIS SYSTEM SPECIFICATIONS

Manufacturer: Ionics, Inc., Aquamite I

Pairs of Membranes: 200

Number of Hydraulic Stages: 6 in series

Stack Dimensions: 40.6 cm long x 24.1 cm wide x 30.5 cm high
(16 in long x 9.5 in wide x 12 in high)

Product Flow: 1.9 m^3/day (500 gal/day at 2500 mg/L TDS feed)

Typical Product TDS: 100 mg/L at 50% recovery, 2500 mg/L TDS feed

% Recovery: 50 percent without brine recycle
80 percent with brine recycle

Polarity Reversal: Once each 15 minutes

Power Characteristics: 120V, Single Phase

Power Consumption: 8 kWhr/1000 gal

Temperature Range: 0-45^{o}C (32-110^{o}F)

Operating Pressure: 311 kPa (45 psig)

Stack Pressure Drop: 173 kPa (25 psig)

pH Range: 1 - 13

Chlorine Tolerance: Cl_2 must be removed

Filter: One 10-um cartridge type

TABLE D5
ELECTRODIALYSIS WITH REVERSAL (EDR): INDEPENDENT AND DEPENDENT VARIABLES TO BE STUDIED DURING NITRATE REMOVAL TESTS

Degree of pretreatment required: original design for only cartridge filtration (10 um) and activated carbon for dechlorination.

pH of product water: continuous monitoring

% water recovery: (product flow/feed flow) 100

% TDS removal: based on conductivity and gravimetric methods

Concentration histories of contaminant in product water: NO_3^-

Concentration histories of common ions in product water: Ca^{++}, Mg^{++}, Na^+, Cl^-, HCO_3^-, $SO_4^=$

*Degree of $CaSO_4$ supersaturation

Pressure drop across membrane stack: monitor only

C_F = concentration of ion in feed
C_P = concentration of ion in product
* = variable not studied in Glendale tests.

Before entering the EDR unit, raw water passed through a granular activated carbon filter F-1E (Figure D4) for dechlorination and then through a protective 10 um cartridge filter F-2E mounted on the outside of the unit. Prior to entering the membrane stack, a portion of the raw water was metered through rotameter R-3E and blended with recycled brine in tank T-1E. The mixture was pumped (P-1E) through filters F-3E and F-4E into the membrane stack through either rotameter R-1E or R-2E. Flow into the stack was controlled by valves built into the rotameters and by the pump recirculating valve V-3E. Flow reversal was achieved by automatic, timed switching of the stack inlet solenoid valves SV-5E and SV-6E and the outlet solenoid valves SV-3E and SV-4E. The hydrogen, oxygen, and chlorine produced in the electrode compartments by the passage of current were vented from the brine recycle tank via a vent pipe to atmosphere above the trailer.

ION EXCHANGE (Figure D5, Tables D6-D7)

The 2 gal/min (8 L/min) ion exchange system was made up of two 8-inch (20.3 cm) and two 10-in (25.4 cm) diameter plexiglass columns which typically contained 3 ft. (0.91 m) of anion or cation exchange resin.

Although single-bed or two-bed ion exchange processes could be simulated with either upflow or downflow exhaustion and regeneration only, single-bed anion-exchange with NaCl regeneration was used in Glendale.

Figure D5 is a process and instrumentation diagram for a two column ion exchange system using column IX-1 and IX-2. A similar system was used with columns AA-1 and AA-2. For exhaustion of a single anion column, raw water was pumped (P-1) from tank T-1 downflow through either column (IX-1 or IX-2) by manipulating valves V-13 and V-14 to control flow and solenoid valves SV-7, 9, 18, and 20 to direct flow through IX-1 or IX-2 into the overflow vessel and finally into one of the collection tanks (T-4 or T-5). The automatic sampler took samples from the overflow vessel at a predetermined time interval, e.g., hourly, and stored them in 500-mL bottles for subsequent analyses and construction of effluent concentration histories of eluted ions.

Backwashing an exhausted column was accomplished with either pressurized raw water (V-1) or pumped (P-1) treated water which had been returned to the feed tank T-1 from one of the treated water storage tanks (T-4 or T-6). To direct the backwash flow through one or the other columns into the overflow vessel and then to waste, electrical solenoid valves SV-17, 19, 7, 9, and 11 were manipulated. In Glendale field tests, 100% bed expansion was observed during backwashing for 5-15 minutes.

The downflow regeneration and displacement rinse flow patterns were from tanks T-3 or T-2 through pumps P-3 or P-2 into and through IX-1 or IX-2 to the overflow vessel where sampling took place. The downflow regenerant and displacement rinse flows were directed using solenoid valves SV-6, 8, 18, and 20. Upflow regeneration was accomplished from tanks T-2 or T-3 using pumps P-2 or P-3 then directing the regenerant flow through IX-1 or IX-2 to the overflow vessel by manipulating SV-6, 8, 10, 17, 19 and 24.

Regenerant solution of the desired concentration for each run was prepared by dissolving the required amount of technical grade NaCl with raw water in tank T-2 or T-3. Complete regeneration required about 4 equivalents salt per equivalent resin. Partial regeneration tests were run using 0.64, 1.0, and 2.0 equivalents salt per equivalent resin. For a roughing regeneration, the spent regenerant from the previous run was collected in tank T-4 and pumped into tank T-2 through pump P-6. A fresh regenerant solution was prepared in tank T-3. After the exhausted resin bed was partially regenerated with spent solution from tank T-2, the fresh regenerant was pumped through the bed at the same flowrate as a polishing step to complete the regeneration.

The usual ion exchange column operating sequence was as follows: exhaustion, backwash, regeneration (upflow or downflow), displacement (slow) rinse, fast rinse, repeat. The fast rinse, not previously described, was accomplished in the same manner as the exhaustion step except that the rinse water was sent to waste rather than treated water storage.

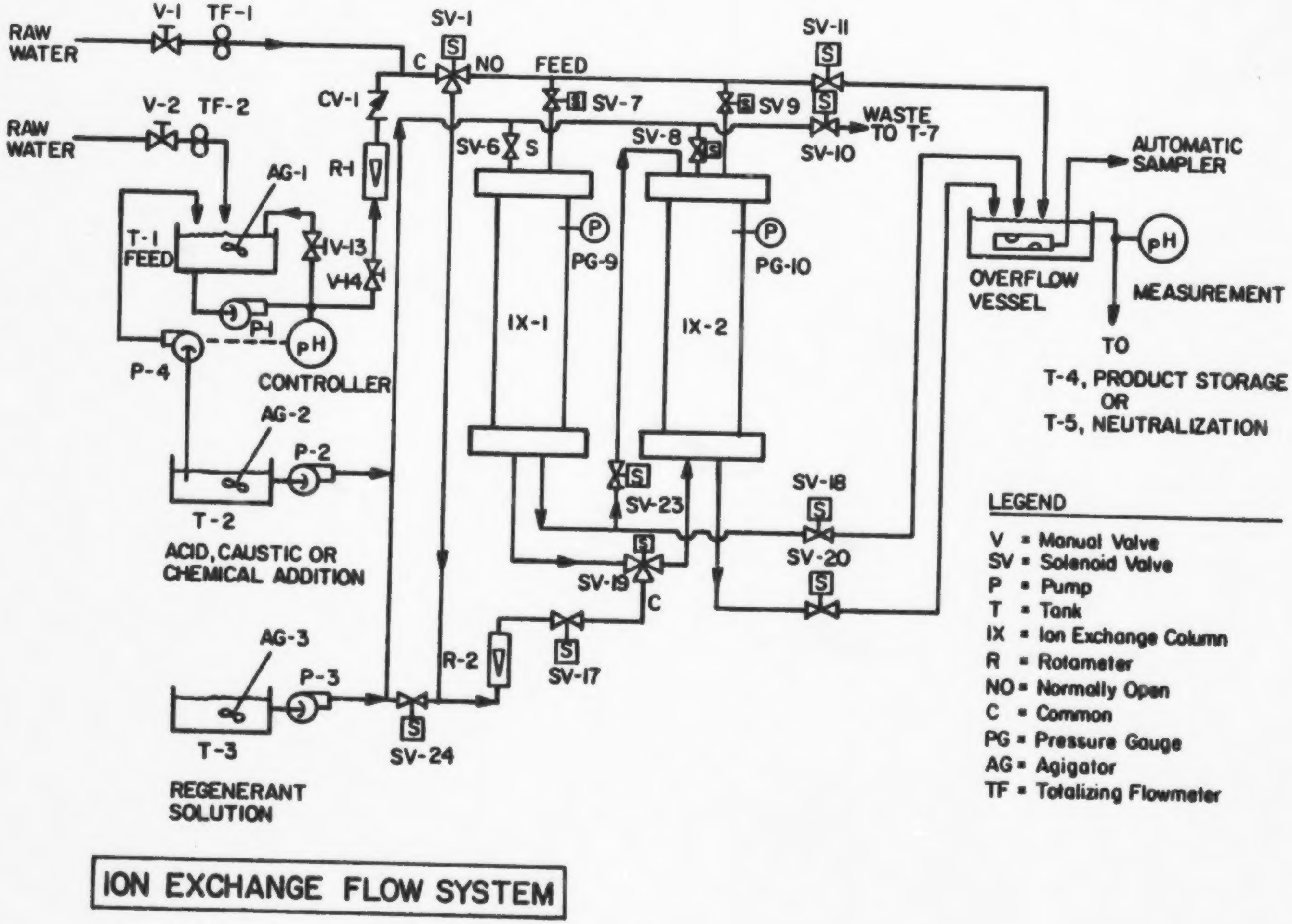
RAW WATER
V-1
TF-1
RAW WATER
V-2
TF-2
SV-1
S
C
NO
FEED
CV-1
R-1
SV-7
SV-6
S
SV-8
SV9
SV-11
SV-10
WASTE TO T-7
AG-1
T-1 FEED
IV-13
V-14
P-1
P-4
pH
CONTROLLER
PG-9
PG-10
IX-1
IX-2
AG-2
P-2
T-2
ACID, CAUSTIC OR CHEMICAL ADDITION
AG-3
P-3
T-3
REGENERANT SOLUTION
SV-24
R-2
SV-17
SV-19
C
SV-23
SV-18
SV-20
OVERFLOW VESSEL
AUTOMATIC SAMPLER
pH
MEASUREMENT
TO
T-4, PRODUCT STORAGE
OR
T-5, NEUTRALIZATION
LEGEND
V = Manual Valve
SV = Solenoid Valve
P = Pump
T = Tank
IX = Ion Exchange Column
R = Rotameter
NO = Normally Open
C = Common
PG = Pressure Gauge
AG = Agigator
TF = Totalizing Flowmeter
ION EXCHANGE FLOW SYSTEM

Figure D-5. Process and instrumentation diagram for the two-column ion exchange (IX) system.

Detailed specifications for the ion exchange system are listed in Table D6 and the variables studied during exhaustion and regeneration are listed in Table D7.

TABLE D6
TYPICAL ION EXCHANGE SYSTEM SPECIFICATIONS

Column height = 6 ft, 1.83 m

Column material = acrylic plastic

Column inside diameter =
AA1 & AA2: 8 in, 20.3 cm; wall thickness = 1/4 in, 0.635 cm
IX1 & IX2: 10 in, 25.4 cm; wall thickness = 1/4 in, 0.635 cm

Depth of media = AA1 & AA2: 2.28 ft, 0.69 m
IX1 & IX2: 3.05 ft, 0.929 m

Column cross-sectional area = AA1 & AA2: 0.349 ft^2, 324 cm^2
IX1 & IX2: 0.525 ft^2, 506 cm^2

Volume of resin = AA1 & AA2: 0.8 ft^3, 22.5 L
IX1 & IX2: 1.6 ft^3, 47 L

Water flow rate = 1.1 gal/min, 4.16 L/min

Column loading = AA1 & AA2: 3.2 gal/ft^2 min, 128 L/m^2 min
IX1 & IX2: 2.1 gal/ft^2 min, 86 L/m^2 min

Empty bed contact time = AA1 & AA2: 5.4 min
IX1 & IX2: 11.3 min

Exhaustion rate = AA1 & AA2: 1.38 gal/ft^3 min, 11.1 BV/hr
IX1 & IX2: 0.69 gal/ft^3 min, 5.3 BV/hr

Anion exchange capacity = 1.33 meq/mL resin for ASB-2

Typical run time = AA1 & AA2: 35 hours
IX1 & IX2: 72 hours

Backwash rate = 3 gal/ft^2 min

Regeneration rate = AA1 & AA2: 0.66 gal/ft^3 min, 0.089 L/L min
IX1 & IX2: 0.33 gal/ft^3 min, 0.043 L/L min

Regenerant contact time = AA1 & AA2: 11.3 min; IX1 & IX2: 23.5 min

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TABLE D6 (continued)

Regeneration time = 60-90 min

Displacement rinse rate = Regeneration rate

Displacement rinse volume = 2 BV

Fast rinse rate = Water flow rate

Fast rinse volume = 10-20 BV

TABLE D7
SINGLE ANION BED ION-EXCHANGE (IX): INDEPENDENT AND DEPENDENT VARIABLES STUDIED DURING NITRATE REMOVAL TESTS

Exhaustion Step

Strong base anion resin characteristics:

(1) Dowex 11, STY-DVB, Quat. Type 1, Isoporous SBA, Alpha S/N = 3.4, Alpha N/Cl = 3.0

(2) Ionac ASB-II, STY-DVB, Quat. Type 2, Gel SBA, Alpha S/N = 3.0, Alpha N/Cl = 3.6

(3) Ionac ASB-I, STY-DVB, Quat. Type 1, Gel SBA, Alpha S/N = 1.87, Alpha N/Cl = 3.0

Number of Columns in Series: 1 or 2 (one column in Glendale)
Media Depth: 0.6 m to 2 m in AA or IX columns
Empty Bed Contact Time: 1 min to 10 min (5-10 min in Glendale)
Effluent Concentration History of Contaminant: NO_3^-
Effluent Concentration Histories of all Common Ions: Cl^-, HCO_3^-, $SO_4^=$
pH of Effluent: continuously monitored
Contaminant Loading on Bed at Contaminant Breakthrough: meq NO_3^-/mL
Degree of Resin Fouling Observed Due to: Fe, Mn, SiO_2

Regeneration Step

Regenerant Flow Direction: downflow or upflow
Regenerant NaCl concentration: 0.25 to 3.0 N (1.5% to 18%)
% Recovery of Ion Exchange Capacity after Regeneration
Stoichiometry of Regeneration: meq regenerant/meq contaminant removed
Quantity and Compostion of Regenerant Produced

Alpha S/N = Sulfate/Nitrate Separation Factor
Alpha N/Cl = Nitrate/Chloride Separation Factor
STY-DVB = Styrene Divinylbenzene
SBA = Strong Base Anion
WBA = Weak Base Anion
Quat. = Quaternary Amine Anion Resin

APPENDIX E

ANALYTICAL DETAILS

Method : Colormetric Nitrate/Nitrogen (NO_3-N)

Apparatus: HACH Low Range Nitrate Test Kit
Model NI-14
Cat. No. 14161-00

Procedure:

(1) Fill one of the color viewing tubes to the mark with the sample to be tested. Stopper and shake vigorously. Empty the tube and repeat the procedure.

(2) Fill the color viewing tube to the mark with the sample (dilution of sample might be required).

(3) Clip open and add the contents of one NitraVer VI Nitrate Reagent Powder Pillow to the sample. Stopper immediately and shake for 3 minutes. Allow the sample to sit undisturbed for an additional 30 seconds .

(4) Pour the prepared sample into a second color viewing tube being careful that the cadmium particles remain in the first tube.

(5) Add the contents of one NitriVer (R) III Nitrite Reagent Powder Pillow to the sample, stopper and shake for 30 seconds. A red color will develop if nitrate is present. Allow at least 10 minutes before completing steps (6) to (8).

(6) Insert the tube containing the prepared sample in the right opening on the top of the color comparator.

(7) Rinse the unoxidized cadmium metal from the color viewing tube used in step (2), fill to the mark with the original water sample, and place in the left opening on thetop ofthe comparator.

(8) Hold the comparator up to a light, such as the sky, a window or a lamp and view through the openings in front. Rotate the color disc until a color match is obtained. Read the mg/L Nitrate-Nitrogen (N) through the scale window.